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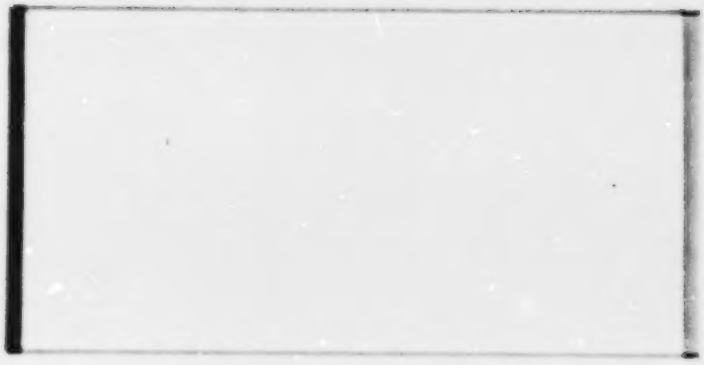

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POLLUTANT LOSSES IN DICHOTOMOUS SAMPLERS

Report No 84-180-K

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ABSTRACT

The three event-type acid precipitation monitoring networks operating in Ontario have utilized different air sampling techniques to measure acidic air pollutants. An early field comparison sponsored by the three network operators revealed that the dichotomous sampler used by Ontario Hydro yielded volatile and particulate nitrate and sulfur dioxide concentrations that were considerably lower than those measured by the Ontario Ministry of the Environment (OME) and the Atmospheric Environment Service (AES) using different samplers. In light of these findings, two studies were undertaken at Ontario Hydro Research: a laboratory study to determine whether volatile nitrate is lost to the various components of the dichotomous sampler, and a field study, covering summer and winter conditions, to compare uncoated and Teflon-coated dichotomous samplers and an OME/AES-type sampling system. The laboratory study showed that gaseous nitric

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acid was lost to the interior surfaces of the dichotomous sampler. The addition of a Teflon-liner to the sampling tube reduced losses of nitric acid. The largest loss of HNO_3 was found to occur inside the virtual impactor. In the field study, the particulate sulfate and ammonium concentrations measured by the three samplers were comparable. The OME/AES-type sampler yielded larger total nitrate concentrations than either of the dichotomous samplers. The particulate and volatile nitrate concentration differences between the OME/AES-type sampler and the two dichotomous samplers were attributed to the volatilization of the additional coarse particulate nitrate collected by the OME/AES-type sampler.

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To Mr. F.J. Kee
Director of Research

POLLUTANT LOSSES IN DICHOTOMOUS SAMPLERS

1.0 INTRODUCTION

Ontario Hydro (OH) voluntarily initiated a sulfate aerosol monitoring program in 1975/1/ in response to concerns over health effects. The monitoring network has undergone several changes since its inception.

In 1981, the sampler used for acidic air pollutant monitoring was changed. Dichotomous air samplers replaced hi-vol and RAC low-vol air samplers to take advantage of improved knowledge and methodologies in the study of sulfate aerosols. At the same time, a shift in emphasis from sulfate aerosol to acid precipitation required that other acidic pollutants, such as nitric acid, nitrate and sulfur dioxide, also be monitored. To accomplish this the dichotomous sampler, originally developed for aerosol sampling, was modified slightly to allow collection of these other pollutants.

A comparison with the Ontario Ministry of the Environment (OME) Acidic Precipitation in Ontario Study (APIOS) event network and the Atmospheric Environment Service (AES) of Environment Canada Air and Precipitation Monitoring Network (APN) was undertaken in 1981. The comparison, undertaken at the APIOS monitoring site at Dorset, Ontario, indicated that the OH results for total nitrate and sulfur dioxide were lower than those obtained by OME and AES/2/.

In order to explore the differences observed in the Dorset comparison, two additional studies were undertaken: (1) a laboratory investigation of gaseous nitric acid losses in the dichotomous sampler and (2) a second field comparison among a dichotomous sampler, a Teflon-coated dichotomous sampler and an OME/AES-type sampling system.

The objectives of the laboratory study were to determine whether nitric acid losses occur in the dichotomous sampler and to determine the relative contribution of the various sampler components to these losses.

The goal of the field study was to compare the OH dichotomous samplers with the OME/AES-type sampling system, under meteorological conditions similar to those encountered in the Dorset comparison. The information obtained from the study would allow a comparison with the Dorset results. In addition, the results may allow us to develop adjustment factors to make data from all three networks comparable.

A review of previous work is given in Section 2.0. The test apparatus assembled to perform the laboratory study and the experimental details for the field comparison are given in Section 3.0. The results of work are given in Section 4.0 and discussed in Section 5.0. Conclusions and recommendations are presented in Sections 6.0 and 7.0, respectively.

2.0 REVIEW OF PREVIOUS WORK

In 1981, a comparison of the air sampling monitoring programs of OH, OME and AES was undertaken. The study was carried out during the winter (February 5 to April 21) and summer (July 15 to October 8) seasons of 1981 at the OME monitoring site at Dorset, Ontario.

Daily air samples were collected according to the procedures followed by the three networks. OH employed a dichotomous sampler with sampling inlet approximately 1 meter above ground level (AGL), to collect sulfate, nitrate and ammonium aerosol; volatile nitrates; and sulfur dioxide. Filter cassettes mounted in the coarse and fine air streams were employed. The volatile nitrates and sulfur dioxide were collected on nylon and potassium carbonate-impregnated cellulose filters, respectively. The latter two filters were separated with a fine mesh, stainless steel screen. The filter cassette was similar to that employed in the OME network. The total sample flow rate was 16.7 L/min and each sample was collected over a 24-hour period. Only particles smaller than 15 µm were sampled by the dichotomous sampler due to particle size fractionation by the aerosol inlet. The incoming air stream passed over a considerable amount of aluminum surface prior to reaching the filter media. The filter analysis techniques and detection limits were comparable to those of the OME and AES networks.

The OME sampling methodology consisted of a single, multi-stage filter cassette inverted and mounted 10 meters AGL. A Teflon filter was used to trap particulate matter, followed by a nylon filter to capture volatile nitrates and then a potassium carbonate-impregnated cellulose filter to capture sulfur dioxide. The three filters were in direct contact. The sample flow rate was 25 L/min and each sample was collected over a 24-hour period. The incoming air was taken directly through the filter media. The aerosol is not fractionated in this case. Under laminar flow conditions, particles smaller than 35 µm should be collected.

AES employed a sampler similar to that used by the OME. The filter cassette was different - a cellulose filter was used to capture sulfate aerosol and total nitrate and a potassium carbonate-impregnated cellulose filter was used for sulfur dioxide collection. The two filters were in direct contact. The filter cassette was inverted and suspended 10 meters AGL. The sample flow rate was 20 L/min and each sample was collected over a 24-hour period. The incoming air was taken directly through the filter media. The aerosol is not fractionated in this case. Under laminar flow conditions, particles smaller than 30 μm should be collected.

The filter media used by all three sampling systems were directly exposed to ambient temperature, relative humidity and wind speed.

Sampling with filters in the cassette configuration is known to provide a reasonably accurate and reliable method for determining total ambient particulate sulfate and inorganic nitrate/3/.

The total sulfate (coarse and fine, see Section 3.1) collected by the OH dichotomous sampler compared favourably with the OME and AES results. The particulate sulfate values measured by OME and AES samplers were found to be approximately equal.

The OME sampler collected about 2.5 times more total nitrate than the OH dichotomous sampler. Similarly, the AES sampler collected about 1.5 times more total nitrate than the OH sampler.

Sulfur dioxide concentrations were not comparable. The OME values were two times higher than the OH values and the AES values were about 1.5 times higher than the OH values/2/.

Possible factors contributing to the poor sampler comparison are as follows:

(a) Difference in inlet heights - 1 meter AGL for the OH sampler and 10 meters AGL for the OME and AES samplers.

(b) Different particulate size ranges sampled - OH sampler collects particles <15 μm in diameter, whereas the OME and AES samplers collect particles as large as 30 to 35 μm in diameter.

(c) Metal surface effects - the OME and AES air samples are taken directly through the filter media, whereas in the OH sampler the incoming air must pass over a significant amount of aluminum surface prior to reaching the filter media.

(d) Moisture effects on the OH filter media - during periods of high relative humidity and cool ambient temperatures (<10°C), moisture would condense on the internal surfaces of the dichotomous sampler and affect the filters.

(e) Difference in filter media and filter packs - OME and OH used similar filter cassettes; however, the OME filters were not separated. AES used a Whatman 40 for aerosol collection. Each agency prepared their own potassium carbonate-impregnated Whatman 41 cellulose filters for sulfur dioxide collection.

(f) Differences in sampling rate - the sampling rates used by each of the agencies were different.

Nitric acid vapour diffuses and sticks to surfaces such as the 2.5 cm diameter inlet tube of the dichotomous sampler. Surfaces such as Teflon, stainless steel, copper, glass, rubber, polyethylene and tygon were evaluated for gaseous nitric acid transmission efficiency by Bowermaster and Shaw/4/. Transmission efficiencies of 100% and 95% were reported for Teflon and stainless steel, respectively. Glass, rubber, polyethylene and tygon were found to absorb as much as 60% of the nitric acid. The transmission efficiency of aluminum was not available.

3.0 EXPERIMENTAL

3.1 Dichotomous Sampler

The original dichotomous sampler, as manufactured by Sierra Instruments Inc, Carmel Valley, California, was composed of two units: a control module and a sampling module. After the first year of operation, the sampler was modified to eliminate the moisture condensation problem and excessive vibration. The two modules were reconstructed into a single, temperature controlled, easily serviced and vibrationally secure unit. An unmodified sampler was used in the Dorset study. Modified samplers were employed in the studies described in this report.

The dichotomous sampler collects particles that are smaller than 15 μm in diameter and then further size separates them into "coarse" (2.5-15 μm) and "fine" (0-2.5 μm) fractions. The sampler components consist of an inlet head, an inlet tube, a virtual impactor and two filter holders. The dichotomous sampler and its principle of operation are presented in Figure 1. The sampler inlet is 2 m AGL in the modified version. The air stream is drawn through the dichotomous sampler with a Thomas pump (Model 727CM39, 5.0 amp) under pneumatic flow control. The field operating procedures for the dichotomous sampler are described in detail elsewhere/5/.

3.2 OME/AES-Type Sampling System

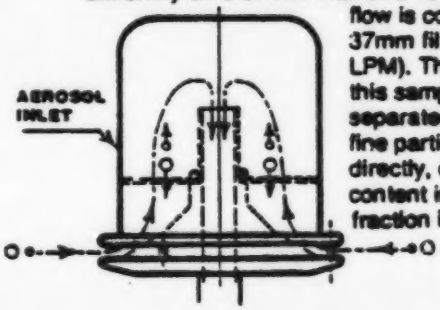
The OME/AES-type sampling system consisted of a multi-stage air filter cassette mounted on a Teflon holder, a protective polyethylene cone, a flow controller and a supporting stand (Figure 2). The sampling assembly (cassette and Teflon holder) and protective polyethylene cone were mounted in an inverted fashion, 2 m AGL on the supporting stand. A Gast model 1550-V138H (250 L/min) pump was used to draw the air stream. The sampling rate was controlled to 16.7 L/min (identical to the total flow rate of the dichotomous sampler) with a Tylan Corporation model FC-202 (50 L/min)mass flow controller.

FIGURE 1

ONTARIO HYDRO DICHOTOMOUS SAMPLER AND THE PRINCIPLE OF OPERATION

PRINCIPLE OF OPERATION

The aerosol (suspended particles and air) enters the aerosol inlet at a flowrate of 1 CMH (16.7 LPM). The unique design of the aerosol inlet deflects the flow vertically upward into the separation chamber where the upward airflow velocity is equal to the sedimentation velocity of a 15 micron particle. Thus, particles larger than 15 microns settle out and do not enter the virtual impactor. The particles smaller than 15 microns are then accelerated through the impactor nozzle of the virtual impactor. By virtue of their greater inertia, particles larger than the 2.5 micron cut-point impact into the "void" of the receiver tube. Thus, the coarse particles impact through a non-existent, or "virtual", surface. To prevent backflow, the receiver tube has a flow rate of 0.1 m^3/hr (1.67 LPM). The coarse particles (15 to 2.5 microns) and 1/10th of the fine particles (less than 2.5 microns) are then collected uniformly on a 37mm filter at a flow rate of 0.1 m^3/hr. The fine-particle flow is collected uniformly on a second 37mm filter at a flow rate of 0.9 m^3/hr (15.0 LPM). The word "dichotomous" is used for this sampler because the particles are separated in the two size fractions. Since the fine particle mass concentration is measured directly, correction for the 10% fine particle content in the coarse particle fraction is precise.



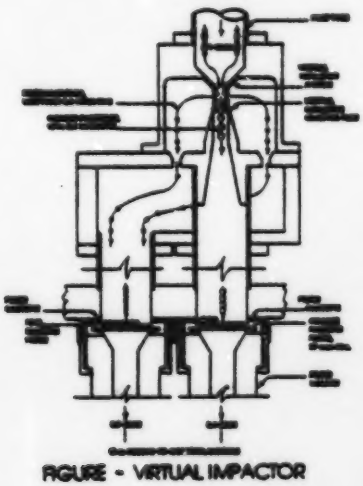
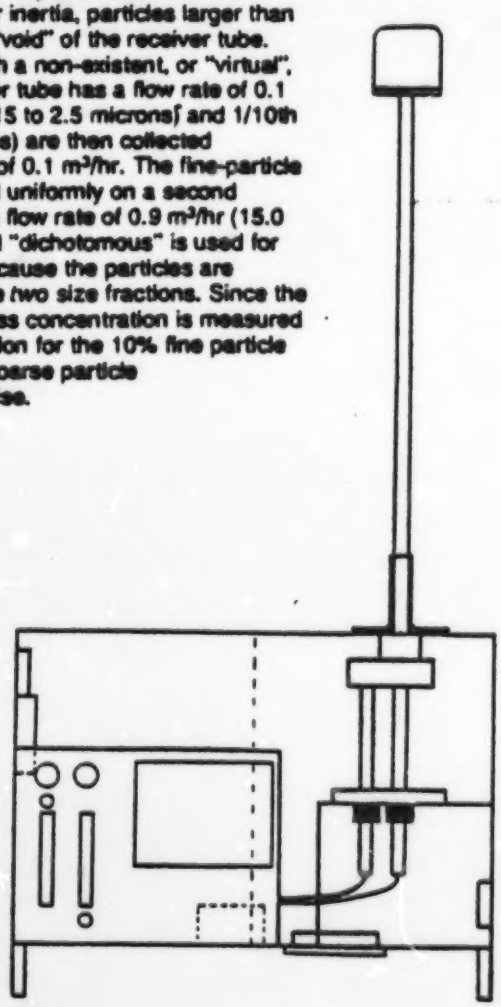


FIGURE - VIRTUAL IMPACTOR



Ontario Hydro Dichotomous Sampler

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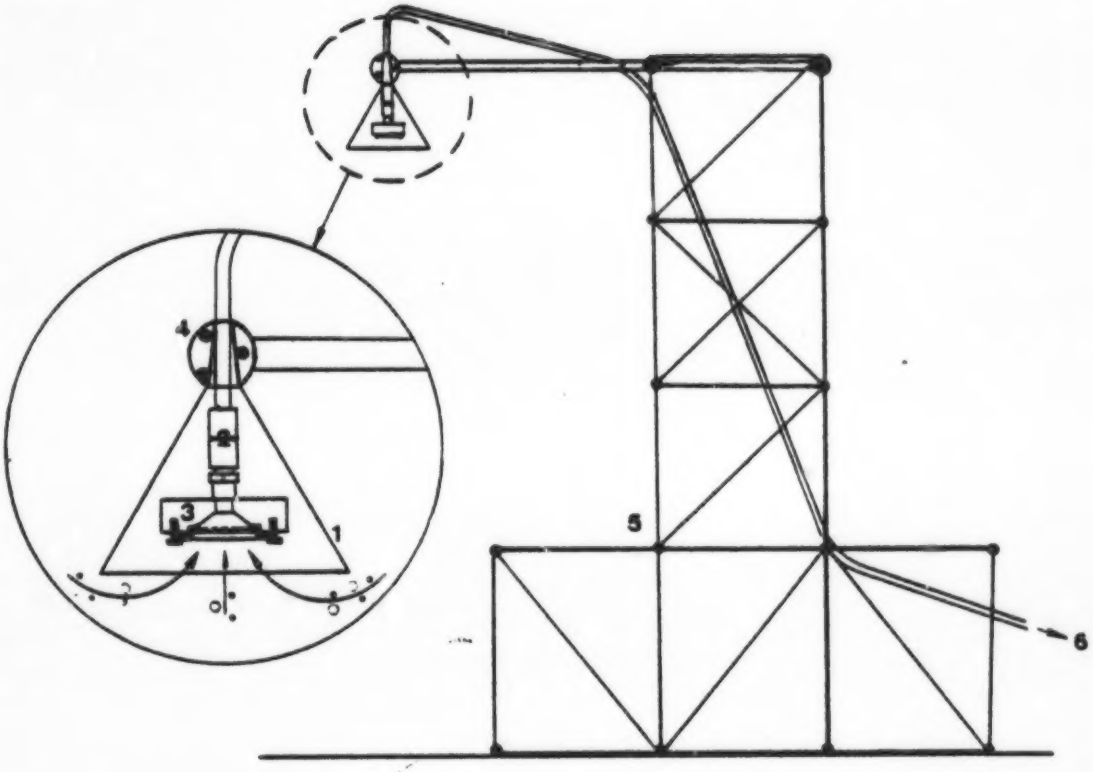
FIGURE 2

OME/AES TYPE AIR AND AEROSOL SAMPLER



1 - Inverted Polyethylene Funnel

2 - Stainless Steel "Quickfit" Connection

3 - Teflon Filter Holder and Filters

4 - Clamp to Hold Funnel and Filter Holder

5 - Aluminum Stand

6 - Exhaust Air to Flow Controller and Pumping System

165060 RD

3.3 Laboratory Apparatus

Figure 3 is a schematic representation of the laboratory apparatus. The sampler inlet head(7) was isolated from the ambient air by a sealed, 0.022 m^3 (22 L), Teflon chamber(6) built at OH Research. This allowed control of the test atmosphere that was sampled by the dichotomous sampler. A reference port(8) was constructed in the wall of the Teflon chamber, diagonally opposite from the inlet manifold(5).

Three pumps(11) were used to draw the air through the reference sampling port. The flow was controlled to 16.7 L/min with a mass flow controller(9). The air stream was drawn from the Teflon chamber through the coarse and fine stream filters of the dichotomous sampler by a Thomas pump(19) under pneumatic flow control(18). The air flows were set separately on the coarse and fine air stream rotameters(16,17).

The test atmosphere containing nitric acid was obtained by mixing saturated vapour from an acid solution of 1 mL HNO_3, 3 mL H_2SO_4 and 46 mL of distilled water/6/, that was stored at room temperature (∿23°C) in a 150 mL Nalgene bottle(3), with air. A 0.9-mm ID, 20-cm long piece of Teflon capillary tubing(4) was used to transport the HNO_3 vapour from just above the acid solution in the bottle(3) to the baffled Teflon inlet manifold(5). The baffles in the manifold provided sufficient turbulence for good mixing of the incoming air stream and the nitric acid vapour. Particulate matter was filtered from the incoming air with an 11-cm OD Whatman 41 cellulose filter mounted in an 11-cm diameter holder(1).

A Matheson model 605 rotameter(2) was used as the standard to set equivalent flows on the reference and total dichotomous sampler air streams. The experiments were conducted at room temperature (∿24°C) and ambient pressure (∿760 mm Hg) with relative humidities in the range of 30% to 40%.

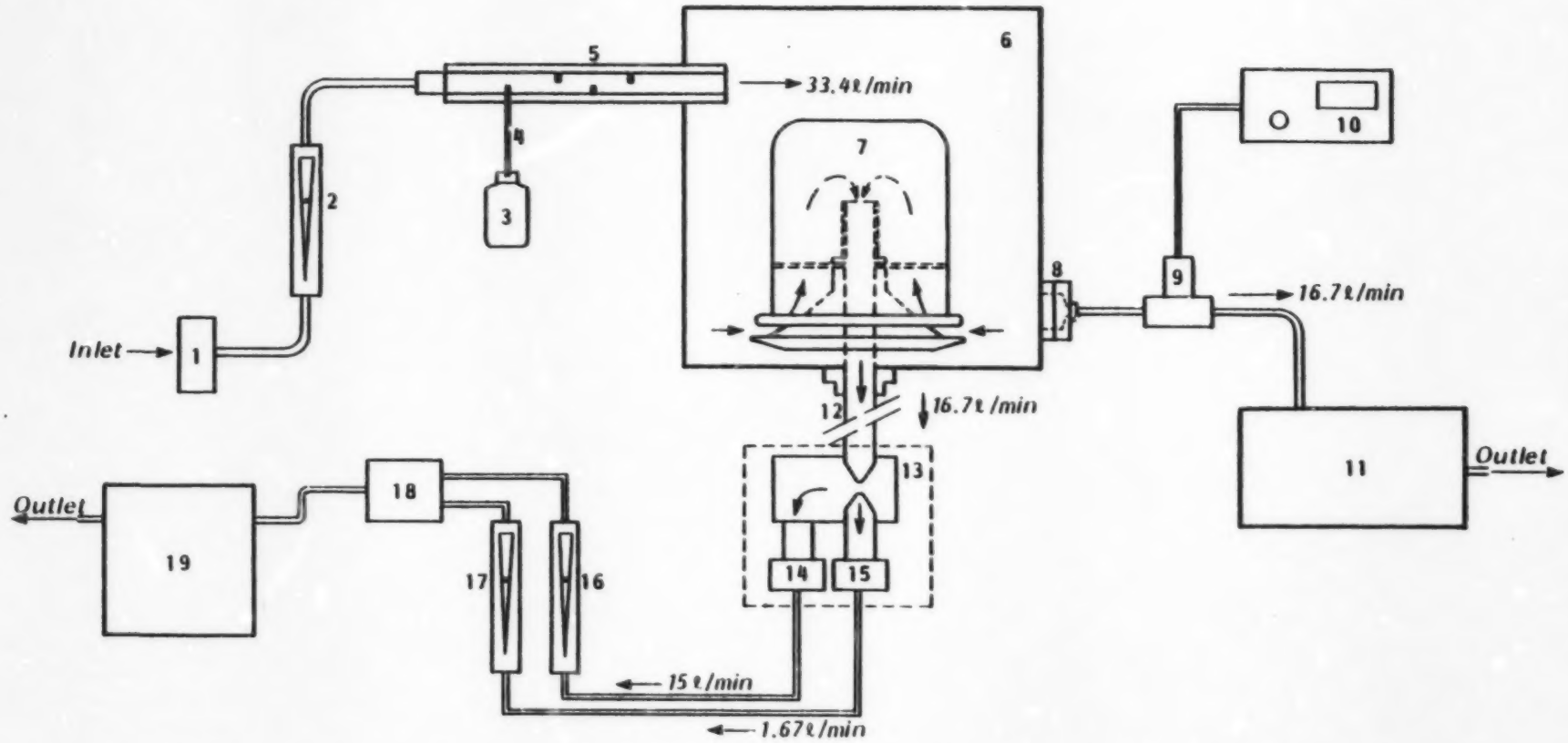
Four sampling configurations were examined:

(a) the dichotomous sampler as used in the OH acid precipitation monitoring network in Ontario;

(b) the sampler inlet head(7) was removed, the inlet tube(12) was lined with thin-walled Teflon tubing and the virtual impactor(3) was retained;

(c) the complete dichotomous sampler with the inlet tube(12) lined with thin-walled Teflon tubing;

(d) the virtual impactor(13) and the coarse and fine filter cassettes (14,15) were removed and were replaced with a single filter cassette that was attached directly to the bottom of the Teflon-lined inlet tube(12).



1 *10cm Diameter Whatman Filter & Holder*
2 *Matheson Model 605 Rotameter*
3 *150ml Nalgene Bottle & HNO_3 Solution*
4 *0.8mm Diameter Teflon Tubing*
5 *Baffled Teflon Inlet Manifold*
6 *0.022m^3 Teflon Chamber*
7 *Aerosol Inlet*
8 *Chamber Filter Cassette Holder*
9 *Tylan Model FC-202 Flow Controller*
10 *Tylan Corp. Model RO-14-220 Readout Box*
11 *3-Thomas Model 607C22, 3.5 Amp Pumps*
12 *Inlet Tube*
13 *Dichotomous Sampling Module (Virtual Impactor)*
14 *Fine Filter Cassette*
15 *Coarse Filter Cassette*
16/17 *Fine & Coarse Sampling Line Rotameters*
18 *Pneumatic Flow Controller*
19 *1 Thomas Model 727CM39, 5.0 Amp Pump*

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FIGURE 3

SCHEMATIC DIAGRAM OF THE LABORATORY APPARATUS USED FOR THE GASEOUS NITRIC ACID LOSSES STUDY

The cassettes consisted of a 37-mm diameter, 1 μm pore size, Teflon filter for non-volatile aerosol removal followed by a 37-mm diameter, 1.1 μm pore size nylon filter for collection of gaseous nitric acid and volatile nitrates.

At least six 24-h samples were collected for each experimental arrangement. A total of thirty-six 24-h samples were collected during the study. Gaseous nitric acid concentrations were determined from analysis of the reference and sampler nylon filters. The analysis methods and detection limits are listed in Table I.

3.4 Field Comparison

A Teflon-coated dichotomous sampler, an uncoated dichotomous sampler and an OME/AES-type sampling system were compared in the field study. The dichotomous and OME/AES-type samplers were described in Sections 3.1 and 3.2.

The air inlets of the three samplers were placed within 3 m of each other on the roof of the Atmospheric Research Laboratory at OH Research. The height of the air inlets of all samplers was set at 2 m above roof-top.

Identical filter cassettes were used with all samplers. Each multi-stage filter cassette consisted of a 37-mm diameter, 1 μm pore size Teflon filter; followed by a 37-mm diameter, 1.1 μm pore size nylon filter for gaseous nitric acid and volatile nitrate collection; and terminated with a 37-mm diameter, potassium carbonate-impregnated Whatman 41 cellulose filter for sulfur dioxide collection. The latter two filters in each cassette were separated with a stainless steel screen. The cassettes were changed daily and submitted for analysis weekly.

Sulfate, nonvolatile nitrate and ammonium aerosol concentrations were determined from Teflon filter analyses. Volatile nitrate concentrations were obtained from nylon filter analyses. The extraction and analysis of potassium carbonate-impregnated cellulose filters provided the sulfur dioxide concentrations. The parameters measured, the analytical methods used/7/ and the detection limits are given in Table I.

Hourly synoptic meteorological information was obtained from Pearson International Airport with the help of the Meteorology Section of the Power System Operation Division of Ontario Hydro. These data were used to help interpret the observed pollutant concentrations.

Twelve concurrent 24-h samples were collected with the three samplers over a four-week summer period (July 26 to August 17, 1983). The three samplers were directly exposed to variations in ambient temperature and other meteorological conditions during the summer sampling.

TABLE I

Pollutants, Analytical Methods and Detection Limits

Pollutant	Analytical Method	Filter Type	Detection Limit (µg/m3)
$SO_4^=$	CFA*	Teflon	0.13
NO_3^- (non-vol)	CFA	Teflon	0.05
NH_4^+	CFA	Teflon	0.05
NO_3^- (vol)	CFA	Nylon	0.05
$SO_4^=$ (SO_2)	CFA	Impregnated**	0.46

* CFA - Continuous Flow Analysis by Technicon Autoanalyser

** Impregnated - Potassium carbonate-impregnated Whatman 41 cellulose filter

Note: Coarse and fine sample stream filters have identical analytical detection limits

Thirteen concurrent 24-h samples were collected with the three samplers over a two-week period (April 7 to 20, 1983). Prior to the availability of the Teflon-coated dichotomous sampler for the comparison, nine concurrent 24-h samples were obtained over a two-week period (February 3 to 17, 1983) with the uncoated dichotomous sampler and the OME/AES-type sampler.

The virtual impactor and the associated filter cassettes of each OH dichotomous sampler were maintained at about 18°C to eliminate moisture accumulation on the filters during wintertime sampling. Previously, the dewpoint of the water in the inlet air was sufficiently depressed by the high dichotomous sampler air flow to cause water to condense on the inside of the sampler. The water would subsequently settle on the filter cassettes and plug the filters. Heating the area around the virtual impactor and the filter cassettes eliminated the moisture problem. The OME/AES-type sampler filter cassette was directly exposed to ambient conditions.

3.5 Nonparametric Sign Test

Differences between each pair of samplers used in the field study were examined with the nonparametric sign test/8,9/ at the 95% confidence level. The sign test provides a quick and simple way of determining whether two sets of paired readings are statistically different. This test does not depend on an assumption of normality; it is applied by testing the sign of the concentration differences for significance. For example, if the uncertainty of each measured concentration is large, then one would expect about one-half of the differences to have positive signs and the remainder to have negative signs. However, if a few of the differences have one or the other sign (eg, 1 negative sign in 12 sample pairs tested), then the test indicates that statistically there exists a difference between the two samplers and that the uncertainty in the measurements is not enough to outweigh the difference.

4.0 RESULTS

4.1 Laboratory Study

The dichotomous sampler is composed of three components: (i) inlet head, (ii) inlet tube and (iii) virtual impactor. Four configurations of the above three components were tested for gaseous nitric acid losses. The ratio (C+F)/REF, total (coarse+fine) volatile nitrate sampled by the dichotomous sampler to the total volatile nitrate collected on the reference filter, should be statistically equal to one in the absence of losses. The inlet gaseous nitric acid concentrations were 1.0±0.5 $\mu g/m^3$. Such concentrations were typical of the annual average concentrations obtained by the OH and OME networks. A few typical annual HNO_3 averages are listed below:

Dorset	1981	OH Sampler	0.55±0.38 $\mu g/m^3$
		OME Sampler	1.38±1.69 $\mu g/m^3$
	1982	OH Sampler	0.40±0.28 $\mu g/m^3$
Mississagi	1982	OH Sampler	0.29±0.22 $\mu g/m^3$

The volatile nitrate ratios, (C+F)/REF, are listed in Table II and displayed in Figure 4.

For configuration (a), the intact dichotomous sampler, an average (C+F)/REF value of 0.08±0.05 was obtained from the first sixteen samples. Approximately thirteen times more nitric acid was reaching the reference nylon filter than was reaching the dichotomous sampler nylon filters. This average (C+F)/REF value indicated that gaseous nitric acid is lost to the internal components of the dichotomous sampler.

The intact dichotomous sampler with the inlet tube lined with thin-walled Teflon tubing was examined in configuration (c). An average (C+F)/REF value of 0.18±0.09 was obtained. The addition of the Teflon lining to the inlet tube reduced the nitric acid loss inside the dichotomous sampler. The (C+F)/REF value increased from 0.08 to 0.18 with the Teflon lining in place.

The inlet head increased the amount of nitric acid lost in the sampler. Without the aerosol inlet the average (C+F)/REF value was 0.30. With the aerosol inlet in place the average (C+F)/REF value decreased to 0.18 and 0.08 (configurations (a) and (b)).

An average (C+F)/REF value of 0.60±0.14 was determined for samples 29 to 36 of configuration (d). In this configuration, the virtual impactor was removed and the inlet head and Teflon-lined inlet tube were retained. A single filter cassette was attached to the exit end of the inlet tube. Removal of the virtual impactor increased the average (C+F)/REF value from 0.08 (complete sampler) and 0.18 (complete sampler + Teflon liner) to 0.60. The virtual impactor appears to be the major source of nitric acid losses.

The fractions of gaseous nitric acid transmitted by each component have been estimated. The inlet head transmits 0.60, the inlet tube 0.44 and the virtual impactor 0.30.

4.2 Field Studies

An OME/AES-type sampler, an uncoated dichotomous sampler and a Teflon-coated dichotomous sampler were compared. The following sampler pairings were made:

Pair A: Teflon-coated dichotomous sampler versus uncoated dichotomous sampler

Pair B: OME/AES-type sampler versus uncoated dichotomous sampler

Pair C: OME/AES-type sampler versus Teflon-coated dichotomous sampler

All three sampling systems were directly exposed to variations in ambient temperature and other meteorological conditions during the summer. During the winter, the virtual impactor along with the coarse and fine particle filter cassettes of the two dichotomous samplers were kept at about 18°C. The OME/AES-type sampler was still directly exposed to variations in ambient temperature and other meteorological conditions during the winter sampling.

TABLE II

Total Volatile Nitrate Concentration Ratios
(Dichotomous Sampler to Reference Filter Cassette)

Sampling Configuration	Sampler No.	Volatile Nitrate Ratio (C+F)/REF	Average Value (C+F)/REF
a	1	0.04 ±0.03	
a	2	0.12 ±0.02	
a	3	0.06 ±0.03	
a	4	0.06 ±0.03	
a	5	0.14 ±0.02	
a	6	0.22 ±0.01	
a	7	0.14 ±0.02	
a	8	0.06 ±0.03	0.08 ±0.05
a	9	0.06 ±0.03	
a	10	0.07 ±0.03	
a	11	0.08 ±0.03	
a	12	0.04 ±0.03	
a	13	0.05 ±0.03	
a	14	0.04 ±0.03	
a	15	0.03 ±0.03	
a	16	0.04 ±0.03	
b	17	0.16 ±0.02	
b	18	0.11 ±0.02	
b	19	0.31 ±0.02	0.30 ±0.13
b	20	0.36 ± 0.02	
b	21	0.40 ± 0.02	
b	22	0.44 ± 0.02	
c	23	0.17 ± 0.02	
c	24	0.09 ± 0.03	
c	25	0.09 ± 0.03	0.18 ± 0.09
c	26	0.16 ± 0.02	
c	27	0.32 ± 0.02	
c	28	0.26 ± 0.02	
d	29	0.43 ± 0.01	
d	30	0.57 ± 0.01	
d	31	0.56 ± 0.01	
d	32	0.55 ± 0.01	0.60 ± 0.14
d	33	0.87 ± 0.01	
d	34	0.70 ± 0.01	
d	35	0.49 ± 0.01	
d	36	0.64 ± 0.01	

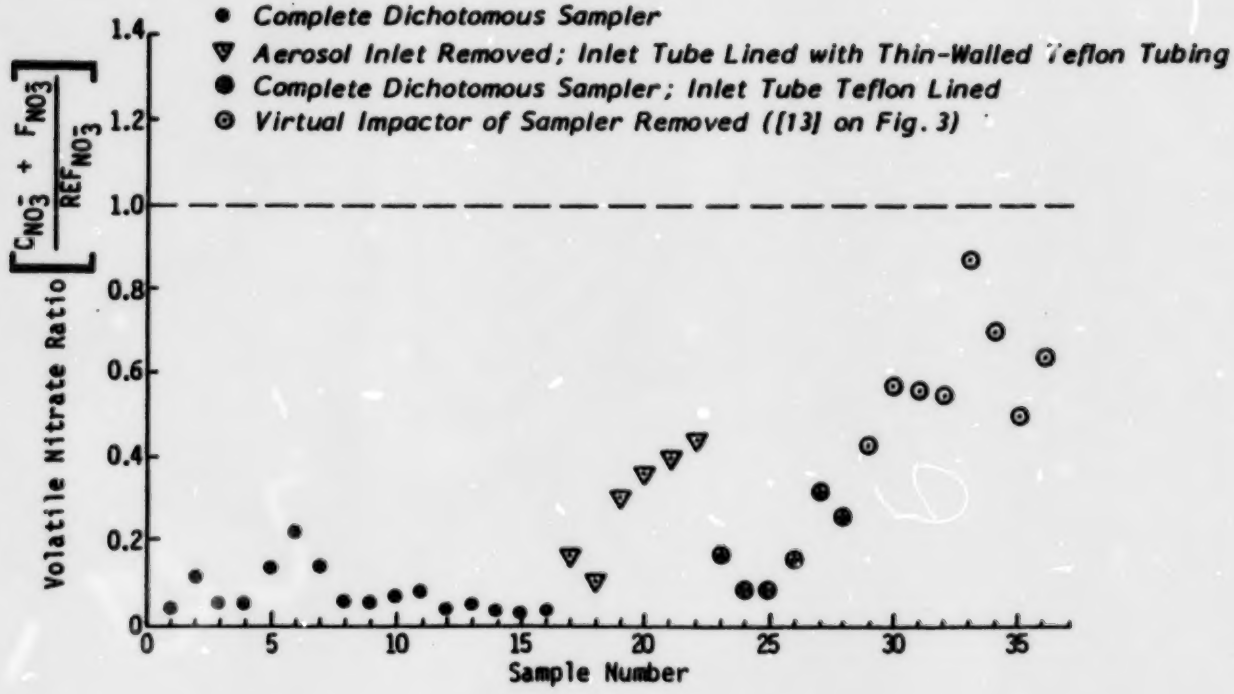

FIGURE 4

RATIO OF TOTAL VOLATILE NITRATE COLLECTED BY DICHOTOMOUS SAMPLER TO TOTAL VOLATILE NITRATE COLLECTED BY REFERENCE FILTER CASSETTE

84-180

164197 RD

Chemical analysis results of Teflon and nylon filters and potassium carbonate-impregnated cellulose filters expressed as concentrations ($\mu g/m^3$) are presented in Tables III, IV and V. The winter, summer and combined results were statistically analyzed. The sign test (Section 2.5) was applied to differences between each pair of samplers. The test results are listed in Table VI. The three data sets were also analyzed by linear regression. The resulting least squares regression line parameters: slope, m, y-intercept, b, and correlation coefficient, r, are summarized in Table VII. The scattergrams, comparing each pair of samplers, are shown in Figures 5 to 10.

The daily meteorological conditions encountered during the field study are summarized in Tables A2 and A3 in the Appendix. The weather phenomena and symbols used in Tables A2 and A3 are listed in Table A1 of the Appendix.

4.2.1 Pair A: Teflon-coated Versus Uncoated Dichotomous Samplers

Pollutant concentration differences (Teflon-coated minus uncoated dichotomous samplers) for the summer and winter sampling periods were determined from the values given in Tables IV and V. The results are listed in Tables A4 and A5 of the Appendix.

The non-parametric sign test was used to evaluate the combined and each of the seasonal data sets for the presence of significant differences. The sign test results for Pair A are listed in Table VI.

The presence of a significant difference, at the 95% confidence level, between the two samplers was not found for coarse, fine and total sulfate, nonvolatile nitrate and ammonium aerosol when the combined data set was tested. For volatile nitrate, sulfur dioxide and total nitrate (volatile +nonvolatile) the sign test did indicate the presence of a significant difference at the 95% and 99% confidence level. For the summer subset, the sign test results were identical to the combined data set results. For the winter subset a significant difference was not found for nonvolatile nitrate aerosol and sulfur dioxide at the 95% confidence level. Scattergrams comparing the concentrations obtained by the two samplers for each pollutant are shown in Figures 5c to 10c.

Linear regression analysis results are listed in Table VII. Teflon-coated and uncoated dichotomous samplers would be statistically equal if the least squares regression line had a slope of one, an intercept of zero and a correlation coefficient of one. For the combined data set, the results indicated that only volatile nitrate concentrations were not similar. For the winter subset, the regression analysis indicated that nonvolatile nitrate and sulfur dioxide concentrations were different, while for the summer subset, nonvolatile and volatile nitrate concentrations were different.

TABLE III

SUMMARY OF AIR POLLUTANT CONCENTRATIONS
MEASURED WITH THE DME/AES-TYPE SAMPLER
(µg/m3)

DATE DDMMYY	= SO4	- NO3 (NON-VOL)	+ NH4	- NO3 (VOL)	SO2	- NO3 TOTAL
30283	3.6	1.4	1.6	1.5	18.8	2.8
70283	4.9	1.8	1.8	2.8	17.4	4.6
80283	2.3	0.87	0.91	0.22	12.5	1.1
90283	3.8	1.4	1.3	0.22	22.2	1.7
100283	2.3	1.0	1.2	0.19	18.3	1.2
140283	14.8	5.7	7.6	3.9	38.4	9.7
150283	11.8	5.9	5.5	1.3	21.3	7.2
160283	12.8	1.0	3.5	4.7	26.7	5.7
170283	4.3	1.1	1.9	1.8	17.7	2.8
70483	9.9	2.9	3.1	2.6	15.2	5.4
80483	4.1	0.66	1.2	1.1	9.65	1.8
90483	3.9	1.2	1.2	0.26	14.1	1.5
110483	6.0	0.67	1.9	1.9	7.36	2.6
120483	2.6	2.7	1.1	1.1	25.0	3.9
130483	6.5	3.8	1.9	0.46	31.5	4.2
140483	7.7	2.5	2.4	0.80	28.9	3.3
150483	5.9	1.1	1.8	1.5	8.13	2.6
160483	3.2	0.80	1.1	0.92	14.6	1.7
170483	1.7	0.32	0.86	1.0	12.5	1.3
180483	3.8	0.41	1.1	0.50	12.6	0.91
190483	3.0	0.32	0.72	0.55	9.75	0.87
200483	3.2	0.25	0.92	0.41	12.8	0.66
260783	1.2	0.52	0.28	2.7	4.50	3.2
270783	5.8	1.7	1.4	3.9	21.9	5.6
280783	21.5	1.6	5.2	7.0	20.4	8.6
20883	3.2	1.2	0.60	2.0	14.7	3.2
30883	11.7	3.5	2.4	3.5	17.9	7.0
40883	24.4	3.6	6.5	6.9	26.4	10.5
80883	2.8	1.2	0.36	1.3	5.27	2.5
90883	0.88	0.51	0.10	0.55	2.86	1.1
100883	4.2	0.89	0.39	0.68	13.5	1.6
150883	9.5	4.2	2.8	4.3	29.3	8.5
160883	25.3	4.1	6.5	9.0	43.4	13.1
170883	32.5	3.2	7.7	8.9	31.6	12.1

TABLE IV

SUMMARY OF AIR POLLUTANT CONCENTRATIONS
MEASURED WITH THE UNCOATED DICHOTOMOUS SAMPLER
(μg/m3)

DATE DDMMYY	= SO4	- NO3 (NON-VOL)	+ NH4	- NO3 (VOL)	SO2	- NO3 TOTAL
30283	3.8	0.21	1.4	1.2	13.7	1.4
70283	4.5	0.58	1.5	1.3	9.55	1.9
80283	2.1	0.41	0.73	0.46	7.81	0.87
90283	2.4	0.42	0.84	0.74	6.04	1.2
100283	1.8	0.22	0.63	0.52	11.4	0.73
140283	16.6	1.4	5.3	4.4	23.6	5.8
150283	12.7	1.3	4.3	3.7	14.9	5.0
160283	12.4	0.75	3.6	2.3	22.0	3.1
170283	4.3	0.23	1.3	0.96	11.0	1.2
70483	9.6	0.43	3.1	2.9	15.2	3.3
80483	3.8	0.21	1.1	0.58	4.71	0.79
90483	3.4	0.32	0.65	0.67	9.46	0.99
110483	5.3	0.17	1.9	1.1	6.56	1.3
120483	2.6	0.81	0.68	1.9	13.9	2.7
130483	5.8	0.91	1.5	2.4	20.3	3.3
140483	7.8	0.54	2.3	1.9	21.9	2.5
150483	5.6	0.31	1.8	0.76	7.86	1.1
160483	3.2	0.23	0.96	0.58	7.42	0.81
170483	3.5	0.18	0.88	0.33	10.3	0.51
180483	3.3	0.13	0.91	0.27	9.19	0.40
190483	2.9	0.10	0.77	0.37	8.09	0.47
200483	3.3	0.13	0.96	0.18	11.3	0.31
260783	2.3	0.32	0.22	0.49	2.75	0.81
270783	5.9	0.99	1.8	0.90	17.0	1.9
280783	24.6	1.5	2.3	1.5	22.7	3.0
20883	2.9	0.78	0.65	0.67	10.9	1.5
30883	15.7	3.1	4.3	2.5	18.2	5.6
40883	19.8	1.4	6.9	2.1	23.0	3.5
80883	3.3	0.57	0.75	0.45	4.70	1.0
90883	1.0	0.050	0.17	0.30	2.50	0.35
100883	4.1	0.41	0.54	0.31	14.2	0.72
150883	9.9	1.9	3.5	2.6	30.3	4.5
160883	24.1	2.4	7.7	1.7	29.3	4.1
170883	31.4	2.7	9.1	1.7	33.0	4.4

TABLE V

SUMMARY OF AIR POLLUTANT CONCENTRATIONS
MEASURED WITH THE TEFLON-COATED DICHOTOMOUS SAMPLER
(μg/m3)

DATE DDMMYY	= SO4	- NO3 (NON-VOL)	+ NH4	- NO3 (VOL)	SO2	- NO3 TOTAL
70483	10.4	0.30	3.1	3.2	22.0	3.5
80483	4.2	0.20	1.2	0.75	7.78	0.95
90483	4.9	0.68	1.2	0.93	19.1	1.6
110483	5.9	0.12	1.9	1.4	8.06	1.5
120483	3.1	1.2	0.77	2.1	20.8	3.3
130483	6.9	1.3	1.8	2.4	19.2	3.7
140483	8.5	0.52	2.5	2.2	30.3	2.7
150483	6.0	0.25	1.8	1.1	7.56	1.3
160483	3.9	0.29	1.1	0.98	8.31	1.3
170483	4.0	0.21	0.98	0.67	11.9	0.88
180483	3.6	0.14	0.95	0.39	8.72	0.53
190483	3.4	0.13	0.82	0.63	8.78	0.76
200483	4.0	0.18	1.1	0.37	10.7	0.55
260783	1.3	0.57	0.22	1.2	3.42	1.8
270783	6.1	1.0	2.0	2.3	18.6	3.3
280783	23.2	1.2	1.4	2.2	24.9	3.5
20883	2.9	0.99	0.60	1.2	11.8	2.2
30883	11.7	1.5	0.65	3.4	18.8	4.9
40883	24.2	1.0	1.5	3.0	25.6	4.0
80883	3.2	0.87	0.71	1.1	5.00	2.0
90883	0.88	1.7	0.21	0.50	2.84	2.2
100883	3.7	0.39	0.54	0.55	13.1	0.94
150883	10.5	2.0	3.6	3.9	30.7	5.9
160883	22.9	2.2	7.1	3.9	43.0	6.1
170883	30.3	2.7	8.7	3.3	33.9	6.0

TABLE VI

Results of Non-parametric Sign Testing of Field Sampling Data

Samplers Compared	Pollutant Compared	Significant Difference at 95% Confidence Level (Yes/No)		
		Combined Data Set	Summer Subset	Winter Subset
Pair A:	Sulfate	No	No	Yes
Teflon-coated Dichotomous Sampler Versus Uncoated Dichotomous Sampler	Nitrate (Non-vol)	No	No	No
	Ammonium	No	No	Yes
	Nitrate (volatile)	Yes	Yes	Yes
	Sulfur Dioxide	Yes	Yes	No
	Total Nitrate (vol + non-vol)	Yes	Yes	Yes
Pair B:	Sulfate	No	No	No
OME/AES-Type Sampler Versus Uncoated Dichotomous Sampler	Nitrate (Non-vol)	Yes	Yes	Yes
	Ammonium	No	Yes	No
	Nitrate (volatile)	Yes	Yes	No
	Sulfur Dioxide	Yes	No	Yes
	Total Nitrate (vol + non-vol)	Yes	Yes	Yes
Pair C:	Sulfate	No	No	Yes
OME/AES-Type Sampler Versus Teflon-coated Dichotomous Sampler	Nitrate (Non-vol)	Yes	Yes	Yes
	Ammonium	No	No	No
	Nitrate (Volatile)	No	Yes	No
	Sulfur Dioxide	No	No	No
	Total Nitrate (vol + non-vol)	Yes	Yes	Yes

TABLE VII

LINEAR REGRESSION ANALYSIS RESULTS FOR EACH PAIR OF SAMPLERS COMPARED AND EACH POLLUTANT MEASURED

Pollutant	Dataset	Pair A			Pair B			Pair C		
		m	b	r	m	b	r	m	b	r
SO_4^-	Combined	0.96	0.52	0.985	0.99	0.12	0.984	1.05	-0.53	0.996
	Winter	1.03	0.55	0.990	0.95	0.50	0.980	0.97	-0.28	0.986
	Summer	0.98	-0.13	0.984	1.03	-0.49	0.981	1.04	-0.32	0.995
NO_3^-	Combined	0.93	0.10	0.962	1.42	0.76	0.702	1.48	0.56	0.787
	Winter	1.42	-0.06	0.938	3.83	-0.14	0.879	2.39	0.33	0.806
	Summer	0.88	0.16	0.933	1.23	0.52	0.858	1.37	0.34	0.661
NH_4^+	Combined	0.93	0.14	0.994	0.89	0.32	0.930	0.89	0.04	0.995
	Winter	0.93	0.23	0.979	1.18	-0.02	0.977	0.96	0.03	0.984
	Summer	0.95	-0.02	0.996	0.84	0.33	0.921	0.90	-0.13	0.998
NO_3^- (vol)	Combined	1.21	0.33	0.905	0.94	1.13	0.404	1.72	-0.42	0.742
	Winter	0.98	0.26	0.995	0.63	0.50	0.613	0.41	0.48	0.539
	Summer	1.38	0.45	0.932	2.20	1.44	0.624	1.86	0.14	0.781
SO_2	Combined	1.03	1.50	0.946	1.04	3.95	0.870	0.91	2.32	0.933
	Winter	1.23	0.24	0.876	1.26	2.77	0.859	0.86	3.47	0.801
	Summer	1.03	0.36	0.996	1.06	0.86	0.934	0.94	1.15	0.987
NO_3^- (Total)	Combined	1.04	0.53	0.938	1.81	0.48	0.860	1.92	-0.70	0.916
	Winter	1.02	0.29	0.990	1.47	0.42	0.967	1.21	0.27	0.940
	Summer	0.93	1.12	0.914	1.93	1.38	0.825	2.06	-0.89	0.896

Note: m = slope, b = y - intercept, r = correlation coefficient
A - Teflon-coated vs regular dichotomous sampler
B - OME/AES vs regular dichotomous sampler
C - OME/AES vs Teflon-coated dichotomous sampler

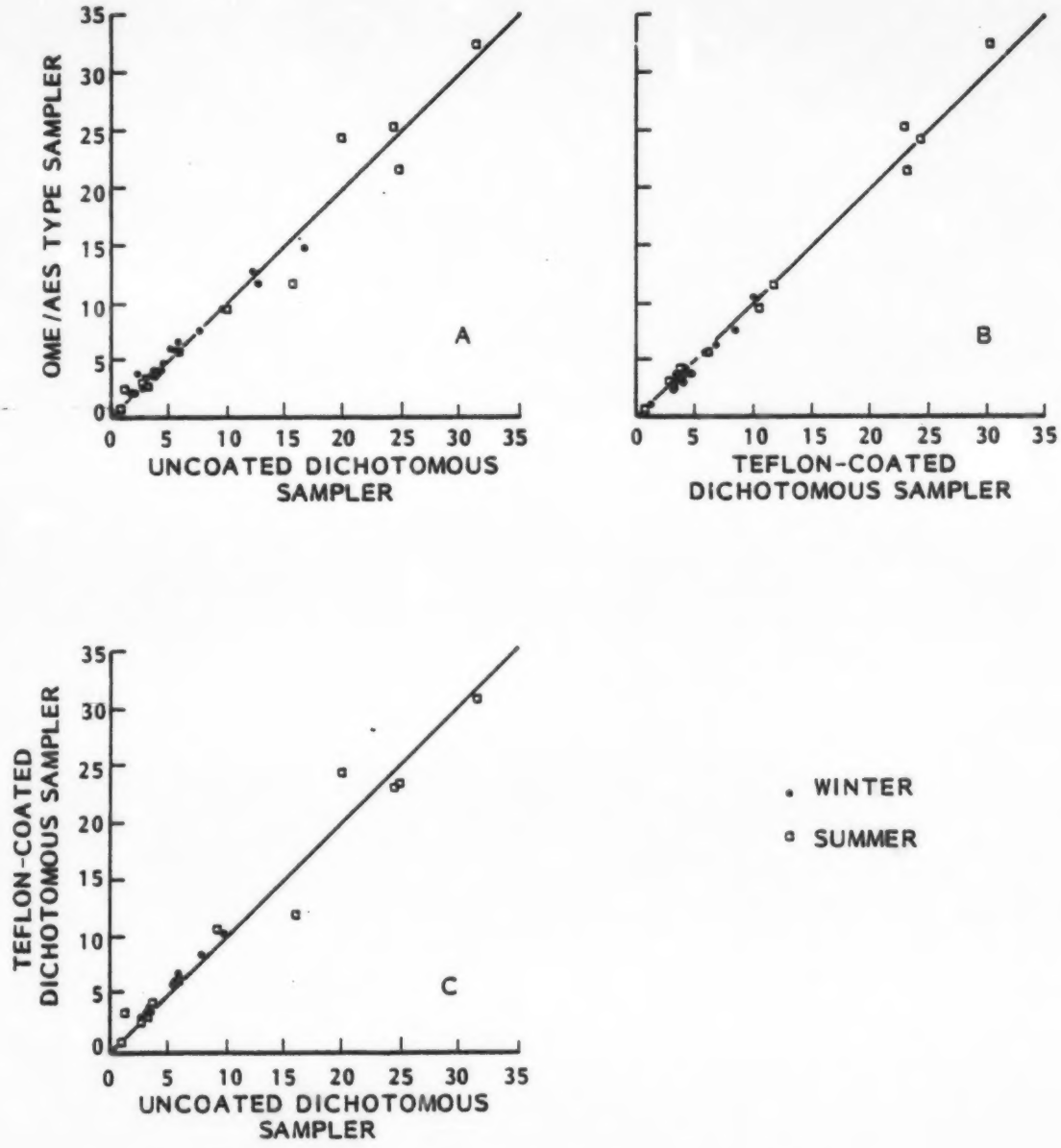

FIGURE 5

AIR SAMPLER COMPARISON:
PARTICULATE SULFATE COLLECTED ON TEFLON FILTERS
KEY: ALL CONCENTRATIONS IN $\mu g/m^3$

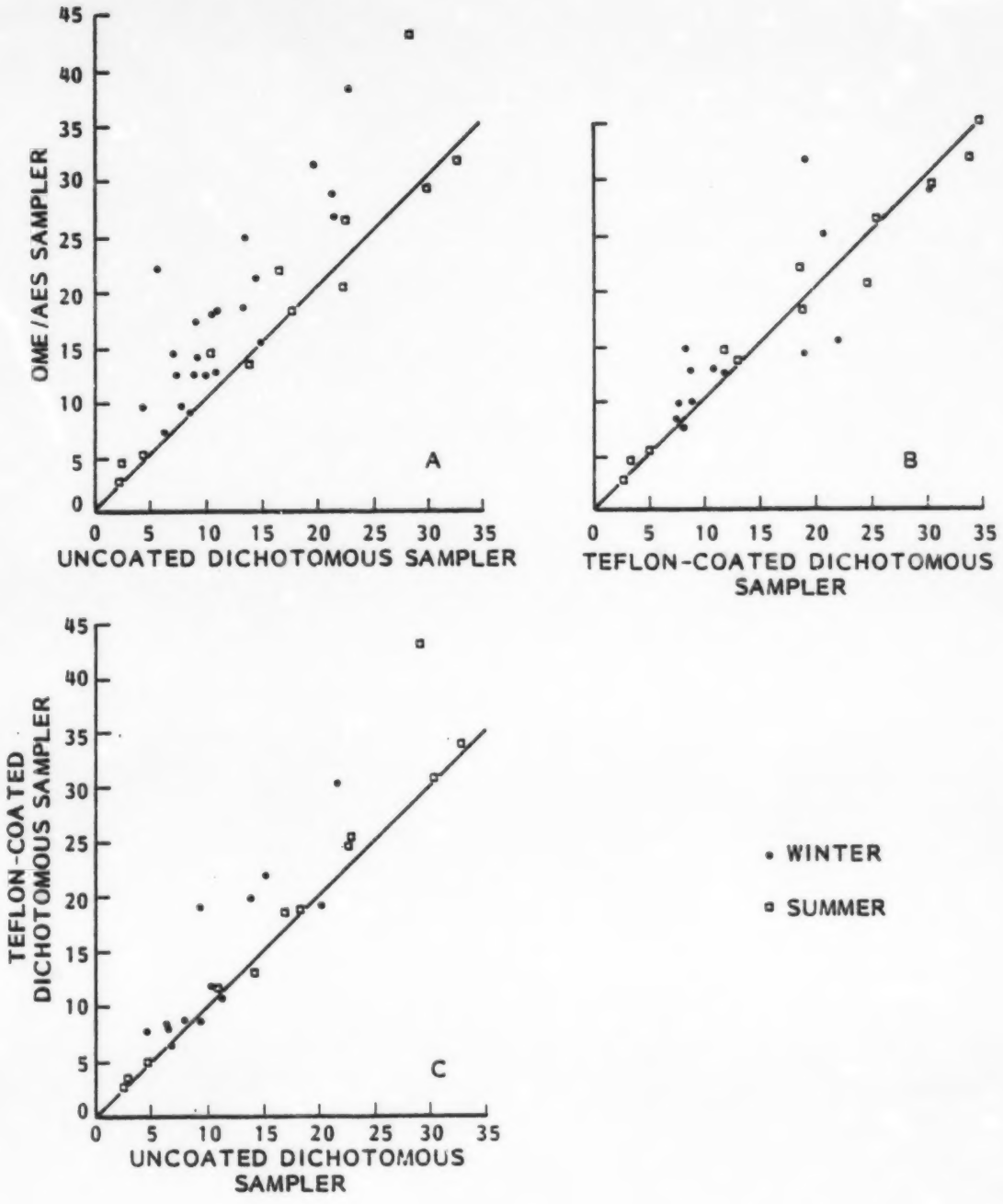

FIGURE 6

AIR SAMPLER COMPARISON:
SULFUR DIOXIDE COLLECTED BY
POTASSIUM CARBONATE IMPREGNATED CELLULOSE FILTER
KEY: ALL CONCENTRATIONS IN $\mu g/m^3$

165064 RD

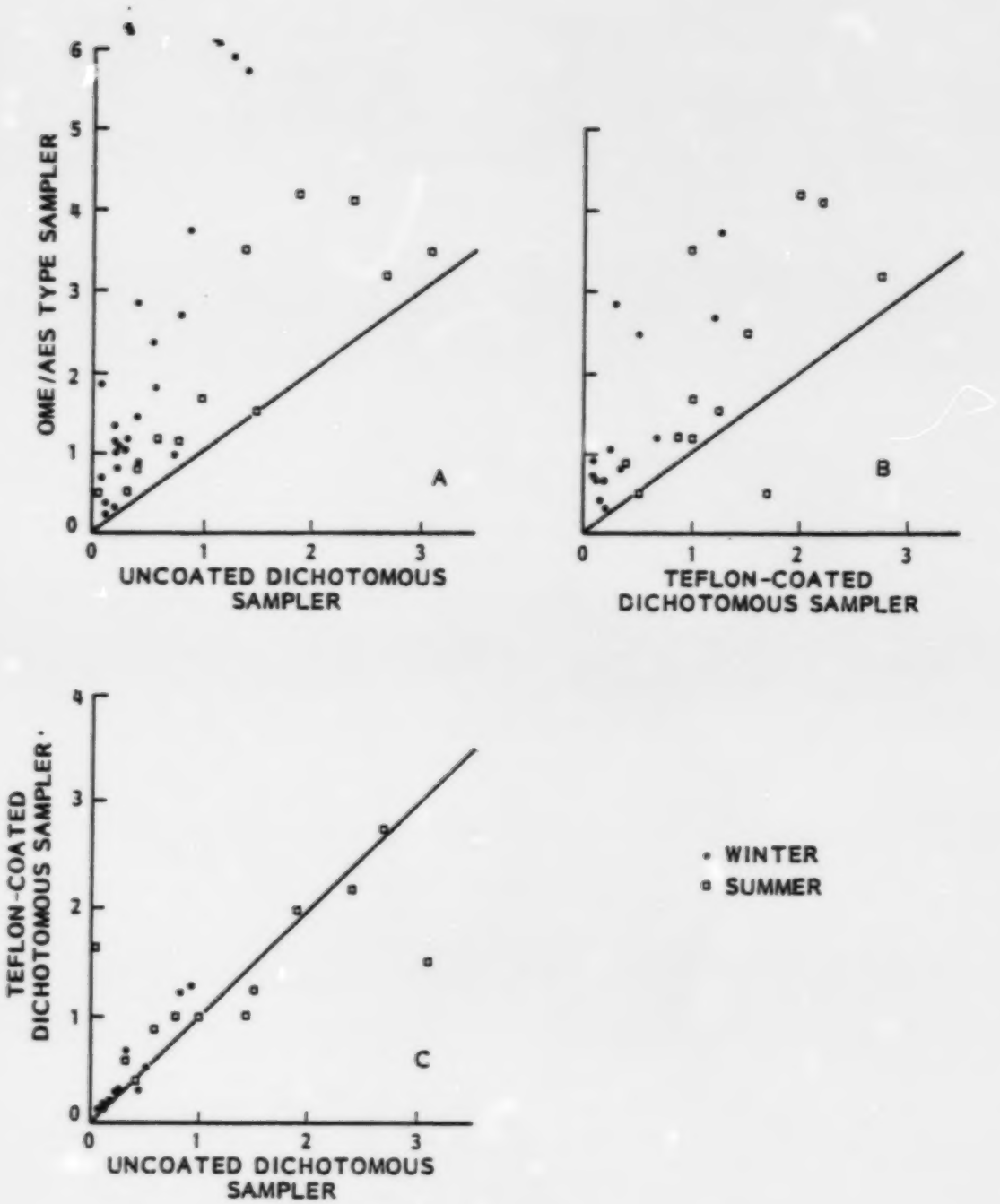

FIGURE 7

AIR SAMPLER COMPARISON:
PARTICULATE NITRATE COLLECTED ON TEFLON FILTERS
KEY: ALL CONCENTRATIONS IN $\mu g/m^3$

165065 RD

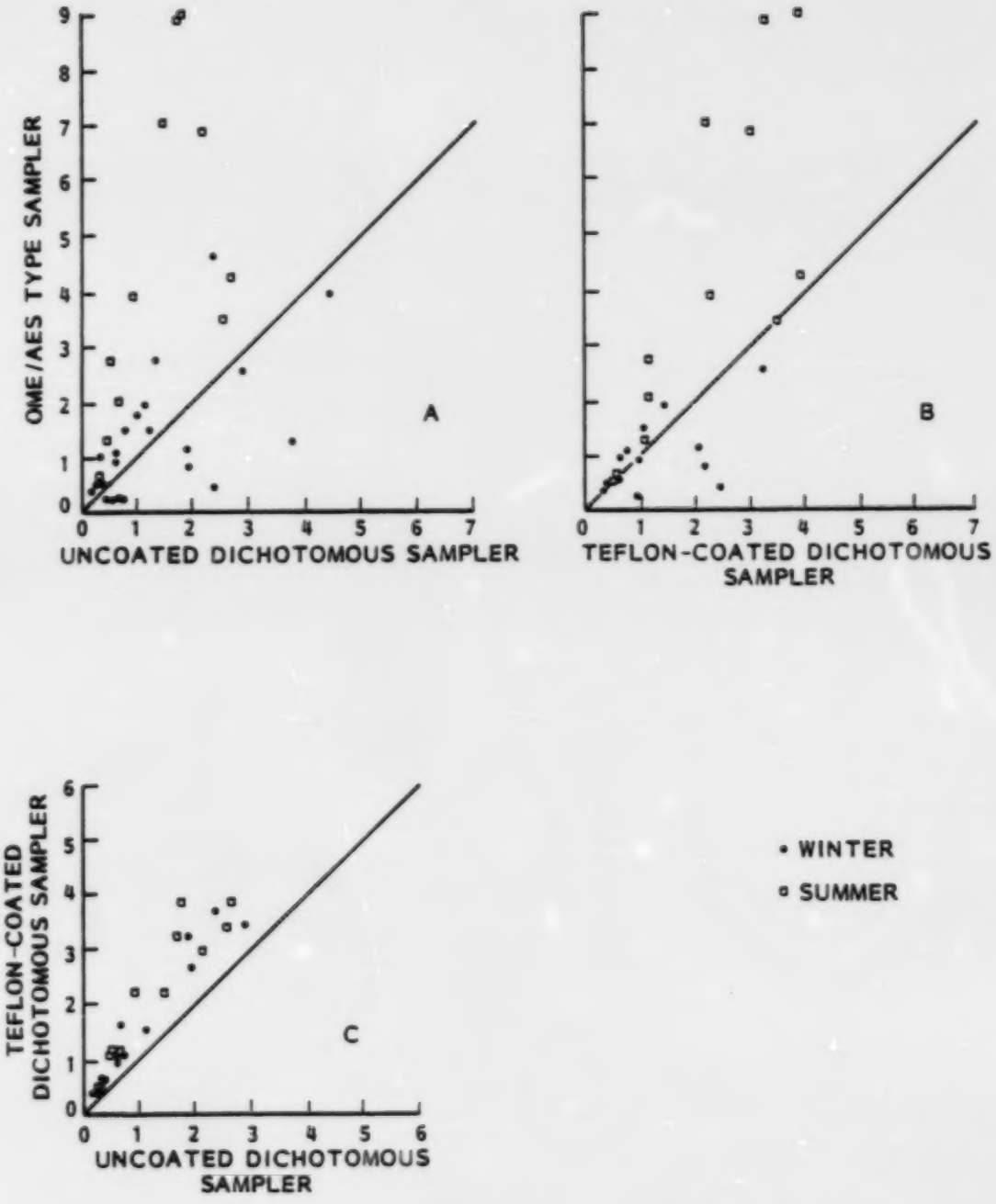

FIGURE 8

AIR SAMPLER COMPARISON:
VOLATILE NITRATE COLLECTED BY NYLON FILTERS
KEY: ALL CONCENTRATIONS IN $\mu g/m^3$

165066 RD

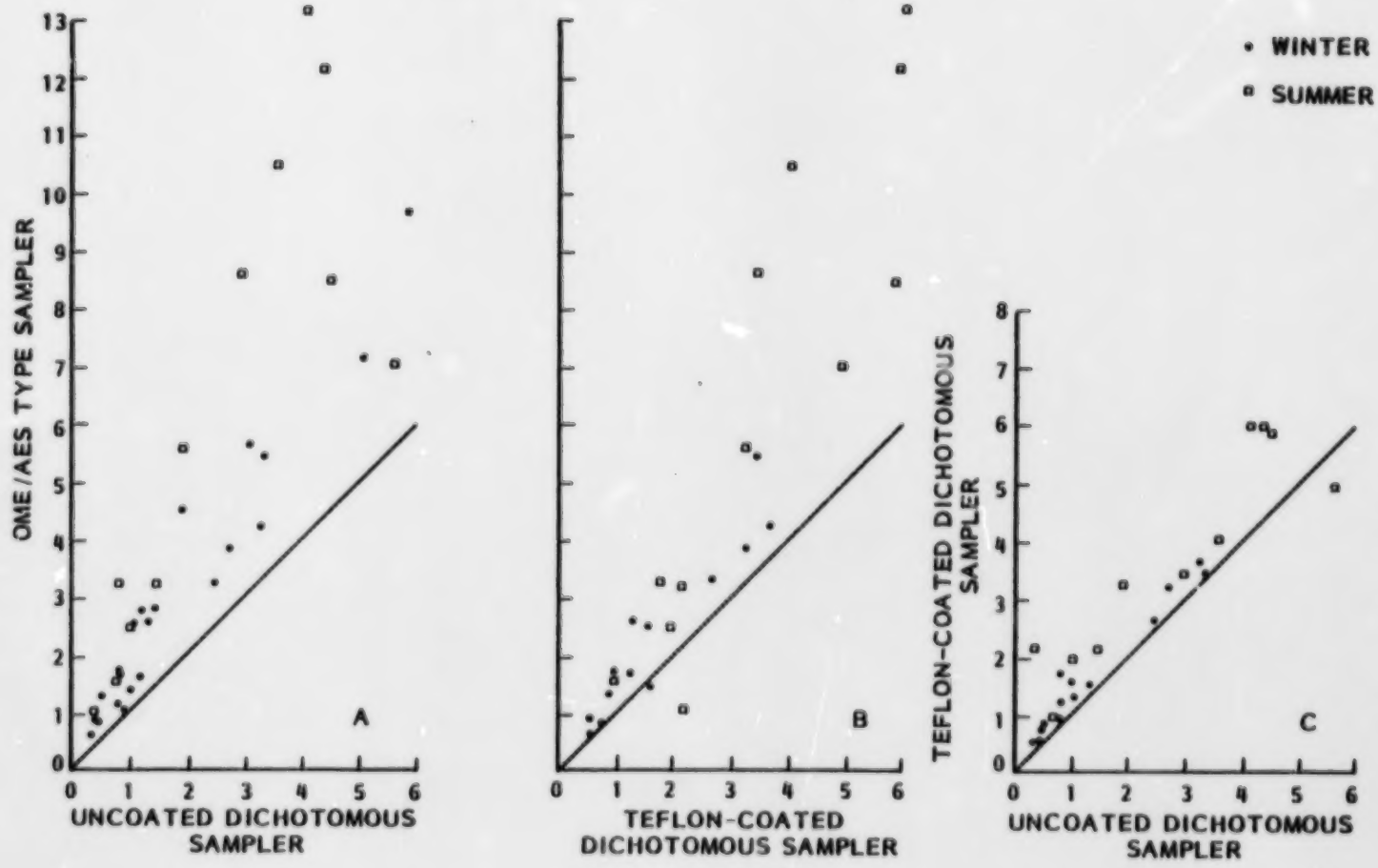

FIGURE 9

AIR SAMPLER COMPARISON:
TOTAL NITRATE COLLECTED ON TEFLON AND NYLON FILTERS
KEY: ALL CONCENTRATION IN $\mu g/m^3$

165067 RD

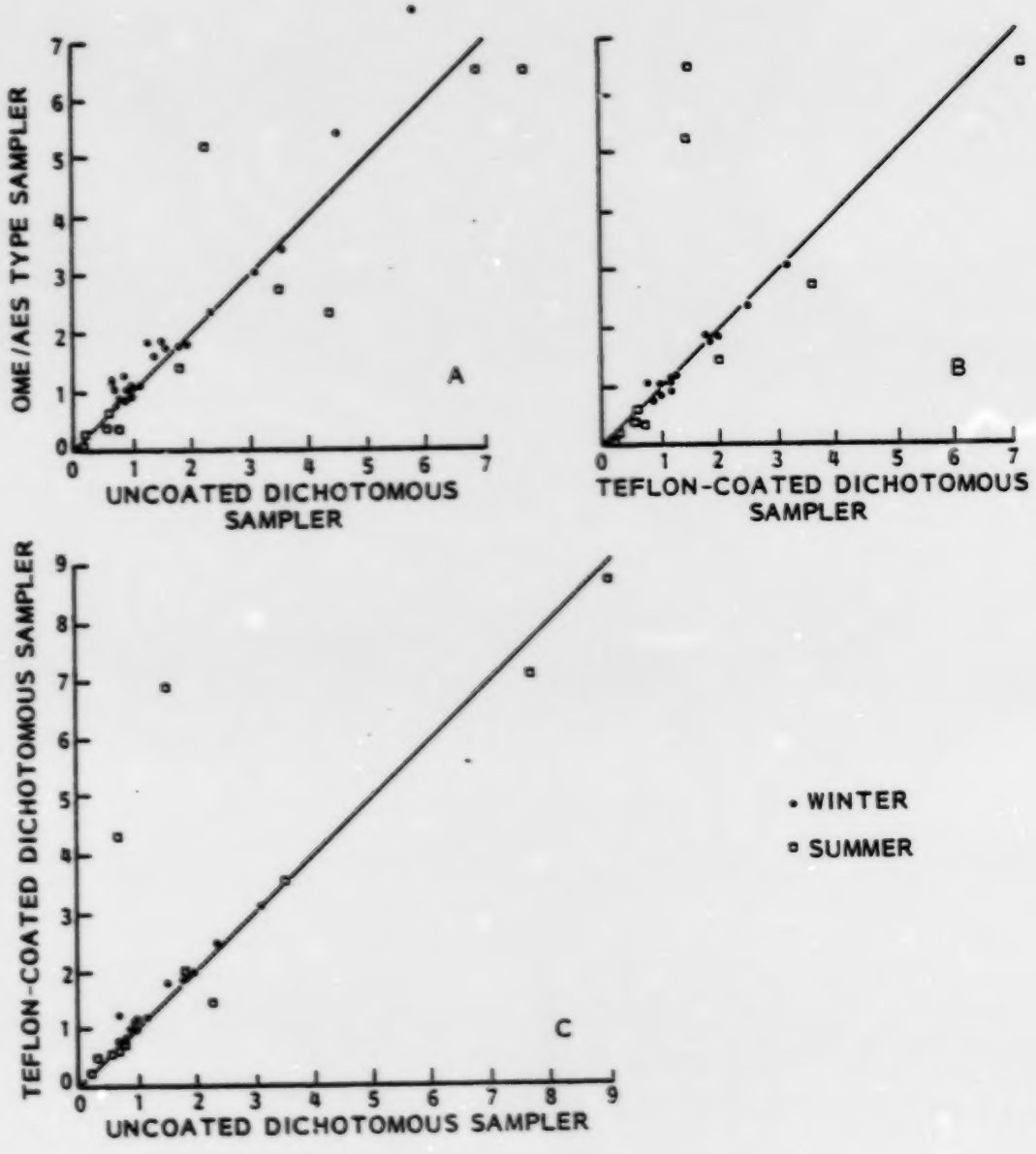

FIGURE 10

AIR SAMPLER COMPARISON:
PARTICULATE AMMONIA COLLECTED ON TEFLON FILTERS
KEY: ALL CONCENTRATIONS IN µg/m3

Correlation coefficients reflect the goodness-of-fit of the regression line, with r=1 indicating a very good fit. Values of r that are <0.85 indicate the presence of significant scatter about the regression line. For Pair A, all the r values were greater than 0.90 with the exception of that for the winter SO_2 data.

Each field sample was collected over a 24-hour period. Pollutant concentration differences, as listed in Tables A4 and A5, were plotted against average daily temperature and wind speed. Correlations with the two meteorological parameters were not detected. The results are shown in Figures A1 to A4 of the Appendix.

4.2.2 Pair B: OME/AES-Type Sampler Versus Uncoated Dichotomous Sampler

Pollutant concentration differences (OME/AES-type sampler minus uncoated dichotomous sampler) were determined from the values given in Tables III and V. The results are listed in Tables A6 and A7 of the Appendix.

For the combined data set, the sign test did not indicate a significant difference between the concentrations of sulfate and ammonium aerosol at the 95% confidence level. For the winter subset, a significant difference was found for nonvolatile nitrate aerosol, sulfur dioxide and total nitrate (volatile + nonvolatile), at the 95% confidence level. For the summer subset, a significant difference was found for nonvolatile nitrate and ammonium aerosol, volatile nitrate and total nitrate (volatile + nonvolatile), at the 95% confidence level. The sign test results are listed in Table VI.

For the pollutants showing significant differences, the difference values were positive indicating that the OME/AES-type sampler was giving the higher values. Scattergrams presented in Figures 6a to 9a visually illustrate the significant differences in sulfur dioxide, and nonvolatile, volatile and total nitrate collected by the two samplers.

Linear regression analysis results are listed in Table VII. For the combined data set, sulfate and ammonium aerosol, volatile nitrate and sulfur dioxide concentrations were comparable. However, a small correlation coefficient was found for the volatile nitrate data indicating a considerable scatter in the data. Only sulfate aerosol concentrations were comparable in the winter study. In the summer comparison sulfate and ammonium aerosol and sulfur dioxide concentrations were comparable.

Comparison of daily temperature and wind speed data with concentration differences for each of the pollutants was undertaken. The results are presented in Figures A5 to A8 of the Appendix. The two meteorological parameters did not correlate with the concentration differences.

4.2.3 Pair C: OME/AES-Type Sampler Versus Teflon-coated Dichotomous Sampler

Pollutant concentration differences (OME/AES-type sampler minus Teflon-coated dichotomous sampler) were determined from the values given in Tables III and IV. The test results for Pair C are listed in Tables A8 and A9 of the Appendix.

The non-parametric sign test was used to test the combined and each of the seasonal data sets for the presence of significant differences between the samplers. The test results are listed in Table VI. The scattergrams shown in Figures 5b to 10b provide a visual comparison of the two samplers.

Significant differences (at the 95% level) were found for particulate nitrate and total nitrate (volatile + nonvolatile) concentrations in the combined data set. The difference is evident in Figures 7b and 9b. In addition, a significant difference was detected for volatile, non-volatile and total nitrate (volatile + nonvolatile) concentrations in the winter data set and sulfate aerosol and nitrate and total nitrate (volatile + nonvolatile) in the summer data set.

Linear regression analysis results are listed in Table VII. The concentrations of sulfate and ammonium aerosol and sulfur dioxide in the combined data set are statistically similar. The same conclusion was obtained for the summer and winter subsets.

Regression analysis for particulate and volatile nitrate concentrations for Pairs B and C yielded small correlation coefficients, consistent with the large scatter in the data. The slopes of the regression lines were significantly greater than one indicating that the OME/AES-type sampler results were not statistically equivalent to the results obtained with the dichotomous sampler.

A comparison of daily average temperature and wind speed with the corresponding pollutant concentration differences was prepared in an attempt to identify any trends that might exist. The results are shown in Figures A9 to A12 of the Appendix. No correlations were detected between the pollutant concentration differences and the two meteorological parameters.

5.0 DISCUSSION

The laboratory results indicate that nitric acid is lost in the dichotomous sampler. The virtual impactor is judged to be the largest contributor to nitric acid losses and the inlet head and inlet tube are also found to contribute significantly to the nitric acid losses. The thin-walled Teflon tubing added to the complete sampler reduced the nitric acid loss in the dichotomous sampler. Nitric acid losses to the Teflon tubing are assumed to be minimal in light of the Bowermaster and Shaw test results/3/. Errors resulting from nitric acid breakthrough on the nylon filters during the 24-hour sampling period at the simulated ambient nitric acid concentrations are known to be negligible/10/.

The Dorset comparison did indicate that the Ontario Hydro sampling system collected significantly lower amounts of particulate and volatile nitrate and sulfur dioxide than the samplers used by the other two agencies. The nitrates and sulfur dioxide concentration differences are thought to have resulted from (a) the difference in height at which the samples were taken; (b) the difference in particle size range that was sampled; (c) filter cassette differences, ie, filter contact and filter type; (d) losses to sampler surfaces and (e) the effect of the different sample flow rates used by the three agencies on artifact nitrate and sulfate formation.

The sampling height difference between the Ontario Hydro sampler and the OME and AES samplers is estimated to lead to a maximum HNO_3 and SO_2 concentration difference of about 10% for neutral atmospheric conditions (worst case)/11,12/. This factor is too small to account for the large differences found during the Dorset comparison.

In the Ontario Hydro field comparison discussed in this report, as many of the above differences as possible were equalized in order to reduce the number of variables to be considered. The sample inlet height for the three samplers was set at two meters. The filters in the filter cassettes were identical in their order, separation and manufacturer production batch. Flow rates and sampling periods were equal. The samplers collected air from the same air mass since the three inlets were separated by only about three meters.

For the Teflon-coated dichotomous sampler and uncoated dichotomous sampler comparison (Pair A), the only physical difference between the two samplers was the material of the interior surface over which the incoming air passed prior to filtration. From the laboratory tests we know that gaseous nitric acid is lost to the interior aluminum surfaces of the dichotomous sampler and that the addition of a Teflon lining reduces the nitric acid losses. An examination of the scattergrams (Figures 5c to 10c) and linear regression results (Table VII) indicates that sulfate, nitrate and ammonium aerosol and sulfur dioxide concentrations measured with the two samplers are comparable.

Volatile nitrate concentrations measured with the Teflon-coated dichotomous sampler were larger than those measured with the uncoated dichotomous sampler. This is consistent with the laboratory results. The volatile nitrate measurements made with the uncoated dichotomous sampler can be corrected to values equivalent to those measured with the Teflon-coated sampler by using the linear regression results of Table VII.

Comparison of the OME/AES-type sampling system with the uncoated or Teflon-coated dichotomous samplers (Pairs B and C) involves two variables: (a) the effect of the dichotomous sampler internal surfaces and (b) the effect of the different particulate size ranges sampled by the OME/AES-type and the dichotomous samplers. At ambient tempertures it is known that up to 50% of the particulate nitrate on a

Teflon prefilter can be volatilized leading to positive errors in the nitric acid measurements/12/. The total nitrate (volatile + nonvolatile), however, would remain accurate and be available for comparison.

The scattergrams and the sign test and linear regression results for Pair C indicate that the OME/AES-type sampler and the Teflon-coated dichotomous sampler are equivalent as sulfate and ammonium aerosol and sulfur dioxide collectors. For total nitrate (volatile + non-volatile) a significant difference between the OME/AES-type sampler and the two dichotomous samplers was indicated by the scattergrams in Figure 9, the sign test results (Table VI) and the linear regression results (Table VII).

The total nitrate concentration differences could result from two sources: (1) absorption of volatile nitrate and the impaction of particulate nitrate on the inner surfaces of the dichotomous sampler and (2) the collection of additional particulate nitrate in the particle size range >15 to <30 μm by the OME/AES-type sampler and the subsequent volatilization of up to 50% of this material/13,14/.

Sulfate and ammonium aerosol are predominantly submicron and are uniformly present throughout the year. However, the particle size distribution of nitrate aerosol is bimodal. Submicron nitrate particles predominate in winter, whereas few are found in summer. The concentration of coarse nitrate particles is significant and present throughout the year/15/.

In light of the bimodal distribution of nitrate aerosol, the volatilization (>50%) of the additional nitrate aerosol that is collected in the >15 to <30 μm size range by the OME/AES-type sampler could lead to substantial increases in both particulate and volatile nitrate concentrations relative to those measured with the dichotomous sampler.

As a comparison, sulfate and ammonium aerosol, both predominantly associated with submicron particles, are sampled in a statistically equal fashion by all three samplers (Figures 5 and 10). If particulate nitrate was predominantly associated with submicron particles then the three samplers should collect particulate nitrate in a statistically equal fashion and the loss of particulate nitrate through volatilization would be comparable, as the sampler flow rates were equal. However, particulate nitrate concentrations are not statistically the same for the three samplers. The OME/AES-type sampler collected more particulate nitrates. The difference in particulate nitrate concentrations likely results from the additional coarse particles that appear to be sampled by the OME/AES-type sampler.

For volatile nitrate the case is not as clear. Coating the dichotomous sampler with Teflon improved volatile nitrate and sulfur dioxide sampling. The testing does not conclusively eliminate the possibility that even with the Teflon coating, volatile nitrate and sulfur dioxide may still be lost in the dichotomous sampler. However, sulfur dioxide

concentration values were statistically equal for the OME/AES-type sampler and the Teflon-coated dichotomous sampler, as shown in Figure 6b and confirmed by the sign test and linear regression results. The same result would be expected for gaseous nitric acid as the two are similar in reactivity. If volatile nitrate is lost to the Teflon-coated sampler then the losses are expected to be small/14/. The majority of the volatile nitrate concentration differences that were observed between the OME/AES-type sampler and the two dichotomous samplers would result from artifact volatile nitrate obtained from volatilization of a portion of the additional coarse particulate nitrate collected.

Sulfate artifact formation in the three samplers would be expected to be comparable and small as sulfate aerosol exists primarily as submicron particles of ammonium sulfate which has a low vapor pressure /16,17/, and the equivalent flow rates of the samplers would contribute an equal amount of artifact to each sampler.

The large HNO_3 and SO_2 concentration differences observed during the Dorset comparison can be considered to result from the following: (a) a small contribution from the height difference; (b) losses to the aluminum inner walls of the dichotomous sampler; (c) losses to moisture trapped on the OH filter cassettes; (d) HNO_3 artifact contributions during sampling; (e) quality control variation of the potassium carbonate-impregnated filters (as each agency prepared their own) and (f) the different sample flow rates used by the three agencies.

6.0 CONCLUSIONS

A number of specific conclusions can be drawn:

1. Significant loss of gaseous nitric acid to the interior surfaces of the dichotomous sampler was found.

2. The largest loss of gaseous nitric acid was found to occur in the virtual impactor component of the dichotomous sampler. The remaining losses occurred in the inlet tube and the inlet head.

3. Teflon lining of the internal aluminum surface of the inlet tube improved the sampling of gaseous nitric acid.

4. Sulfate, nitrate and ammonium aerosol and sulfur dioxide concentrations measured with the two dichotomous samplers were statistically equivalent.

5. Sulfate and ammonium aerosol and sulfur dioxide concentrations measured with the OME/AES-type sampler and the Teflon-coated dichotomous sampler were statistically equivalent.

6. The OME/AES-type sampler was found to collect more particulate and volatile nitrate (total nitrate) than either of the dichotomous samplers.

7. Correlations with average daily temperature and wind speed were not observed for any of the measured pollutant concentration differences between the three pairs of samplers.

8. The particulate, volatile and total nitrate concentrations differences observed between the OME/AES-type sampler and the two dichotomous samplers were attributed to the additional coarse particulate nitrate sampled by the OME/AES-type sampler and to the partial volatilization of this material.

9. Sulfur dioxide sampling by the OME/AES-type sampler and the dichotomous sampler were statistically equal after the addition of the Teflon coating to the inner surfaces of the dichotomous sampler. A similar result was expected for volatile nitrate; however, the results were clouded by artifact volatile nitrate from the partial volatilization of the additional coarse particulate nitrate collected by the OME/AES-type sampler.

10. The observed particulate and volatile nitrate and sulfur dioxide concentration differences observed during the Dorset comparison were thought to be a combination of the following parameters: (a) a small contribution from the sampling inlet height difference; (b) losses to the inner aluminum surfaces of the dichotomous sampler; (c) losses to excess moisture trapped on the dichotomous sampler filter cassettes; (d) the different particle size ranges sampled by the three agencies; (e) quality control of the potassium carbonate-impregnated filters, as each agency prepared their own, and (f) the different sample flow rates used by each agency and the effect this has on artifact nitrate formation during sampling.

7.0 RECOMMENDATIONS

Ontario Hydro's acid precipitation monitoring program was terminated in May, 1983. The results of the present study, therefore, cannot be fully applied. Nonetheless, the following general recommendations are made:

1. Future monitoring of volatile pollutants should be undertaken with instruments that minimize the contact of the sampled pollutant gases with reactive surfaces prior to absorption on the filter media.

2. The particle size range and the sampling flow rate should be comparable to those used by other agencies to facilitate a straightforward comparison of air pollutant data.

3. The volatile and particulate nitrate and sulfur dioxide data collected with the dichotomous sampler should be used for trend analysis. Corrected data must be used for quantitative determinations. Corrections for volatile nitrate and sulfur dioxide concentration losses in the uncoated dichotomous sampler can be made with the linear regression results for the Pair A comparison listed in Table VII.

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APPENDIX

TABLE A1

Weather and Obstructions to Vision
Weather Phenomena and Symbols

General Category	Specific Phenomenon	Symbol
Tornadoes and Thunderstorms	Tornado	Tornado
	Waterspout	Waterspoud
	Funnel Cloud	Funnel Cloud
	Thunderstorm	T, T+
Precipitation	Rain	R--, R-, R, R+
	Rain Shower	RW--, RW-, RW, RW+
	Drizzle	L--, L-, L, L+
	Snow	S--, S-, S, S+
	Snow Grains	SG--, SG-, SG, SG+
	Ice Crystals	IC
	Ice Pellets	IP--, IP-, IP, IP+
	Ice Pellet Showers	IPW--, IPW-, IPW, IPW+
	Snow Showers	SW--, SW-, SW, SW+
	Snow Pellets	SP--, SP-, SP, SP+
	Hail	A--, A-, A, A+
Obstruction to Vision (6 miles or less visibility)	Fog	F
	Ice Fog	IF
	Haze	H
	Smoke	K
	Blowing Snow	BS
	Blowing Sand	BN
	Blowing Dust	BD
	Dust Haze	D

Symbol Representation: -- very light, - light, (blank) moderate, + heavy
(ie) R-, light rain

TABLE A2

Daily Meteorological Data for Dichotomous Sampler Versus OME/AES-Type Sampler - Summer Comparison

Date DDMMYY	Wind Speed Avg (km/h)	Max	Min	Wind Direction	Precip. Type	(h)	Relative Humidity Max (%)	Min	Temperature Avg (°C)	Max	Min
260783	7	15	0	SE-NE	clear		71	32	22	28	14
270783	9	20	0	S-N	clear		72	27	25	31	17
280783	16	28	4	SE-N	TRW	7	88	39	25	29	23
020883	8	26	0	N-SW	clear		93	37	22	28	15
030883	9	19	0	S-N	RW	3	94	42	25	29	21
040883	5	11	0	NE-S	TRW	1	100	73	22	25	21
080883	18	33	4	W-NW	RW	2	93	38	23	34	16
090883	14	24	0	NW-N	clear		93	40	16	22	10
100883	15	28	6	E-N	TRW	5	93	49	20	20	17
150883	4	17	0	S-NE	clear		93	50	20	25	14
160883	7	20	0	SE-NE	clear		88	47	22	28	17
170883	8	17	0	SE-N	clear		94	65	24	27	21

TABLE A3

Daily Meteorological Data for Dichotomous Sampler Versus OME/AES-Type Sampler - Winter Comparison

Date DDMMYY	Wind Speed Avg (km/h)	Max	Min	Wind Direction	Precip. Type	(h)	Relative Humidity Max (%)	Min	Temperature Avg (°C)	Max	Min
030283	20	33	15	SW-NW	SW-S-	18	92	72	-1	4	-8
070283	17	24	6	N-NW	S-	8	92	62	-5	-4	-9
080283	21	26	11	NW-N	SW	2	85	63	-9	-3	-14
090283	12	17	7	N	clear		84	66	-15	-13	-19
100283	17	28	7	NE	SW	9	85	56	-12	-9	-14
140283	7	11	4	W-NW	F	12	100	60	2	5	0
150283	5	17	0	NW-SE	F-FR	19	100	75	3	5	1
160283	9	17	0	SE-S	F-FR	18	100	80	3	4	2
170283	9	31	0	N-NW	clear		86	79	1	4	-3
070483	11	20	0	NW	FR	5	100	71	7	15	1
080483	17	35	6	N-E	clear		92	60	4	8	0
090483	28	44	13	E-SE	FR	18	100	49	7	9	6
110484	17	26	0	NW	RW	4	93	61	5	9	2
120483	13	31	0	N-SE	F	1	93	53	5	10	1
130483	16	33	0	E-SE	FR	6	93	57	7	9	6
140483	20	28	0	SE-SW	FRW	9	100	66	10	12	6
150483	14	30	6	W	clear		80	65	3	6	1
160483	12	24	2	W-N	SW	1	86	52	1	5	-3
170483	24	39	13	N	SW	8	92	60	2	5	-2
180483	17	30	6	NW-N	S	1	86	58	0	2	-3
190483	27	39	6	N	SW	4	92	38	1	4	-2
200483	24	39	4	N-W	clear		86	52	3	7	1

TABLE A4

COMPARISON OF UNCOATED AND TEFLON-COATED DICHOTOMOUS SAMPLERS
(SUMMER COMPARISON)
POLLUTANT CONCENTRATION DIFFERENCES (TEFLON-COATED MINUS UNCOATED)
ORDERED BY DECREASING DAILY AVERAGE TEMPERATURE
(µg/m3)

DATE DDMMYY	TEMP (°C)	WIND SPEED (km/h)	$SO_4^=$	NO_3^- (NON-VOL)	NH_4^+	NO_3^- (VOL)	SO_2	NO_3^- TOTAL
280783	25	16	-1.4	-0.26	-0.82	0.88	2.18	0.51
270783	25	9	0.25	0.01	0.18	1.4	1.67	1.4
30883	25	9	-4.0	-1.6	-3.7	0.92	0.67	-0.67
170883	24	8	-1.1	0.04	-0.32	1.6	0.95	1.6
80883	23	18	-0.08	0.30	-0.05	0.64	0.30	0.94
20883	22	8	0.04	0.21	-0.05	0.50	0.95	0.70
160883	22	7	-1.2	-0.19	-0.58	2.2	13.7	2.0
260783	22	7	-1.1	0.25	0.00	0.67	0.67	0.92
40883	22	5	4.4	-0.40	-5.4	0.88	2.64	0.48
100883	20	15	-0.42	-0.02	0.00	0.24	-1.12	0.22
150883	20	4	0.59	0.11	0.05	1.3	0.40	1.4
90883	16	14	-0.07	1.6	0.04	0.20	0.34	1.8

TABLE A5

COMPARISON OF UNCOATED AND TEFLON-COATED DICHOTOMOUS SAMPLERS
(WINTER COMPARISON)
POLLUTANT CONCENTRATION DIFFERENCES (TEFLON-COATED MINUS UNCOATED)
ORDERED BY DECREASING DAILY AVERAGE TEMPERATURE
(µg/m3)

DATE DDMMYY	TEMP (°C)	WIND SPEED (km/h)	= SO4	- NO3 (NON-VOL)	+ NH4	- NO3 (VOL)	SO2	- NO3 TOTAL
140483	10	20	0.76	-0.02	0.14	0.24	8.42	0.22
70483	7	11	0.76	-0.13	0.01	0.29	6.79	0.15
90483	7	28	1.5	0.36	0.57	0.26	9.59	0.62
130483	7	16	1.1	0.36	0.28	0.07	-1.09	0.43
120483	5	13	0.46	0.41	0.09	0.16	6.88	0.57
110483	5	17	0.67	-0.05	0.02	0.29	1.50	0.24
80483	4	17	0.41	-0.01	0.05	0.17	3.07	0.16
200483	3	24	0.75	0.05	0.19	0.19	-0.56	0.24
150483	3	14	0.37	-0.06	0.06	0.29	-0.30	0.23
170483	2	24	0.55	0.03	0.10	0.34	1.65	0.37
160483	1	12	0.66	0.06	0.18	0.40	0.89	0.46
190483	1	27	0.47	0.05	0.05	0.26	0.69	0.31
180483	0	17	0.33	0.01	0.05	0.12	-0.47	0.13

TABLE A6

COMPARISON OF OME/AES-TYPE SAMPLER AND UNCOATED DICHOTOMOUS SAMPLER
(SUMMER COMPARISON)
POLLUTANT CONCENTRATION DIFFERENCES (OME/AES-TYPE MINUS UNCOATED)
ORDERED BY DECREASING DAILY AVERAGE TEMPERATURE
(µg/m3)

DATE DDMMYY	AVERAGE TEMP (°C)	AVERAGE WIND (km/h)	= SO4	- NO3 (NON-VOL)	+ NH4	- NO3 (VOL)	SO2	- NO3 (TOTAL)
280783	+25	+16	-3.13	+.06	+3.00	+5.60	-2.29	+5.66
270783	+25	+9	-.08	+.70	-.37	+3.01	+4.99	+3.70
30883	+25	+9	-4.02	+.42	-1.97	+.96	-.22	+1.38
170883	+24	+8	+1.12	+.51	-1.32	+7.24	-1.37	+7.75
80883	+23	+18	-.45	+.61	-.40	+.86	+.57	+1.47
20883	+22	+8	+.26	+.38	-.04	+1.35	+3.77	+1.73
160883	+22	+7	+1.20	+1.76	-1.21	+7.30	+14.05	+9.06
260783	+22	+7	-1.17	+.20	+.06	+2.24	+1.75	+2.44
40883	+22	+5	+4.53	+2.12	-.40	+4.77	+3.40	+6.89
100883	+20	+15	+.04	+.48	-.16	+.36	-.71	+.85
150883	+20	+4	-.33	+2.32	-.75	+1.65	-.93	+3.97
90883	+16	+14	-.07	+.46	-.08	+.25	+.37	+.70

TABLE A7

COMPARISON OF ORE/AES-TYPE SAMPLER AND UNCOATED DICHOTOMOUS SAMPLER
(WINTER COMPARISON)
POLLUTANT CONCENTRATION DIFFERENCES (ORE/AES-TYPE MINUS UNCOATED)
ORDERED BY DECREASING DAILY AVERAGE TEMPERATURE
(μg/m3)

DATE DDMMYY	AVERAGE TEMP (°C)	AVERAGE WIND (km/h)	= SO_4	- NO_3 (NON-VOL.)	+ NH_4	- NO_3 (VOL.)	SO_2	- NO_3 (TOTAL)
140483	+10	+20	-.08	+1.95	+.04	-1.12	+6.99	+.83
70483	+7	+11	+.26	+2.43	-.02	-.31	+.04	+2.12
90483	+7	+28	+.46	+.88	+.51	-.41	+4.65	+.47
130483	+7	+16	+.67	+2.85	+.37	-1.90	+11.24	+.96
120483	+5	+13	-.00	+1.92	+.37	-.75	+11.06	+1.16
110483	+5	+17	+.72	+.51	-.07	+.81	+.80	+1.31
80483	+4	+17	+.37	+.45	+.03	+.53	+4.94	+.98
200483	+3	+24	-.10	+.13	-.03	+.23	+1.55	+.35
150483	+3	+14	+.29	+.76	+.02	+.75	+.27	+1.51
150283	+3	+5	-.91	+4.58	+.97	-2.48	+6.37	+2.10
160283	+3	+9	+.44	+.27	-.08	+2.31	+4.70	+2.58
140283	+2	+7	-1.88	+4.32	+1.75	-.49	+14.86	+3.84
170483	+2	+24	+.13	+.14	-.02	+.67	+2.26	+.80
160483	+1	+12	+.00	+.57	+.16	+.34	+7.15	+.91
190483	+1	+27	+.10	+.24	-.06	+.18	+1.65	+.42
170283	+1		+.00	+.84	+.58	+.79	+6.69	+1.63
180483	+0	+17	+.52	+.28	+.14	+.23	+3.42	+.51
30283	-1	+20	-.14	+1.14	+.28	+.30	+5.05	+1.44
70283	-5	+17	+.39	+1.20	+.24	+1.47	+7.81	+2.67
80283	-9	+21	+.17	+.45	+.15	-.24	+4.70	+.21
100283	-12	+17	+.58	+.78	+.58	-.33	+6.95	+.46
90283	-15	+12	+1.41	+1.00	+.43	-.52	+16.14	+.49

TABLE A8

COMPARISON OF ONE/AES-TYPE SAMPLER AND TEFLON-COATED DICHOTOMOUS SAMPLER
(SUMMER COMPARISON)
POLLUTANT CONCENTRATION DIFFERENCES (ONE/AES-TYPE MINUS TEFLON-COATED)
ORDERED BY DECREASING DAILY AVERAGE TEMPERATURE
(µg/m3)

DATE DDMMYY	AVERAGE TEMP (°C)	AVERAGE WIND (km/h)	= SO4	- NO3 (NON-VOL)	+ NH4	- NO3 (VOL)	SO2	- NO3 (TOTAL)
280783	+25	+16	-1.70	+.32	+3.82	+4.83	-4.48	+5.14
270783	+25	+9	-.32	+.69	-.55	+1.65	+3.32	+2.34
30883	+25	+9	-.03	+2.01	+1.70	+.04	-.90	+2.06
170883	+24	+8	+2.22	+.47	-1.00	+5.67	-2.32	+6.14
80883	+23	+18	-.37	+.32	-.35	+.22	+.27	+.54
20883	+22	+8	+.22	+.17	+.00	+.86	+2.82	+1.03
160883	+22	+7	+2.43	+1.95	-.63	+5.15	+.39	+7.10
260783	+22	+7	-.09	-.05	+.06	+1.57	+1.08	+1.52
40883	+22	+5	+.15	+2.53	+5.02	+3.88	+.76	+6.41
100883	+20	+15	+.47	+.50	-.16	+.12	+.42	+.62
150883	+20	+4	-.92	+2.21	-.80	+.38	-1.33	+2.60
90883	+16	+14	+.00	-1.15	-.11	+.05	+.03	-1.10

TABLE A9

COMPARISON OF ONE/AES-TYPE SAMPLER AND TEFLON-COATED DICHOTOMOUS SAMPLER
(WINTER COMPARISON)
POLLUTANT CONCENTRATION DIFFERENCES (ONE/AES-TYPE MINUS TEFLON-COATED)
ORDERED BY DECREASING DAILY AVERAGE TEMPERATURE
(μg/m3)

DATE DDMMYY	AVERAGE TEMP (°C)	AVERAGE WIND (km/h)	= SO4	- NO3 (NON-VOL)	+ NH4	- NO3 (VOL)	SO2	- NO3 (TOTAL)
140483	+10	+20	-.84	+1.97	-.10	-1.35	-1.43	+.61
70483	+7	+11	-.50	+2.57	-.04	-.60	-6.75	+1.97
90483	+7	+28	-.99	+.52	-.06	-.67	-4.94	-.15
130483	+7	+16	-.37	+2.49	+.09	-1.97	+12.32	+.52
120483	+5	+13	-.46	+1.51	+.28	-.92	+4.19	+.59
110483	+5	+17	+.05	+.56	-.09	+.52	-.70	+1.07
80483	+4	+17	-.04	+.45	-.01	+.36	+1.86	+.81
200483	+3	+24	-.85	+.08	-.22	+.03	+2.11	+.11
150483	+3	+14	-.08	+.81	-.04	+.46	+.57	+1.28
170483	+2	+24	-.42	+.10	-.12	+.33	+.61	+.44
160483	+1	+12	-.66	+.51	-.02	-.06	+6.26	+.46
190483	+1	+27	-.38	+.19	-.10	-.08	+.97	+.11
180483	+0	+17	+.19	+.26	+.09	+.11	+3.89	+.38

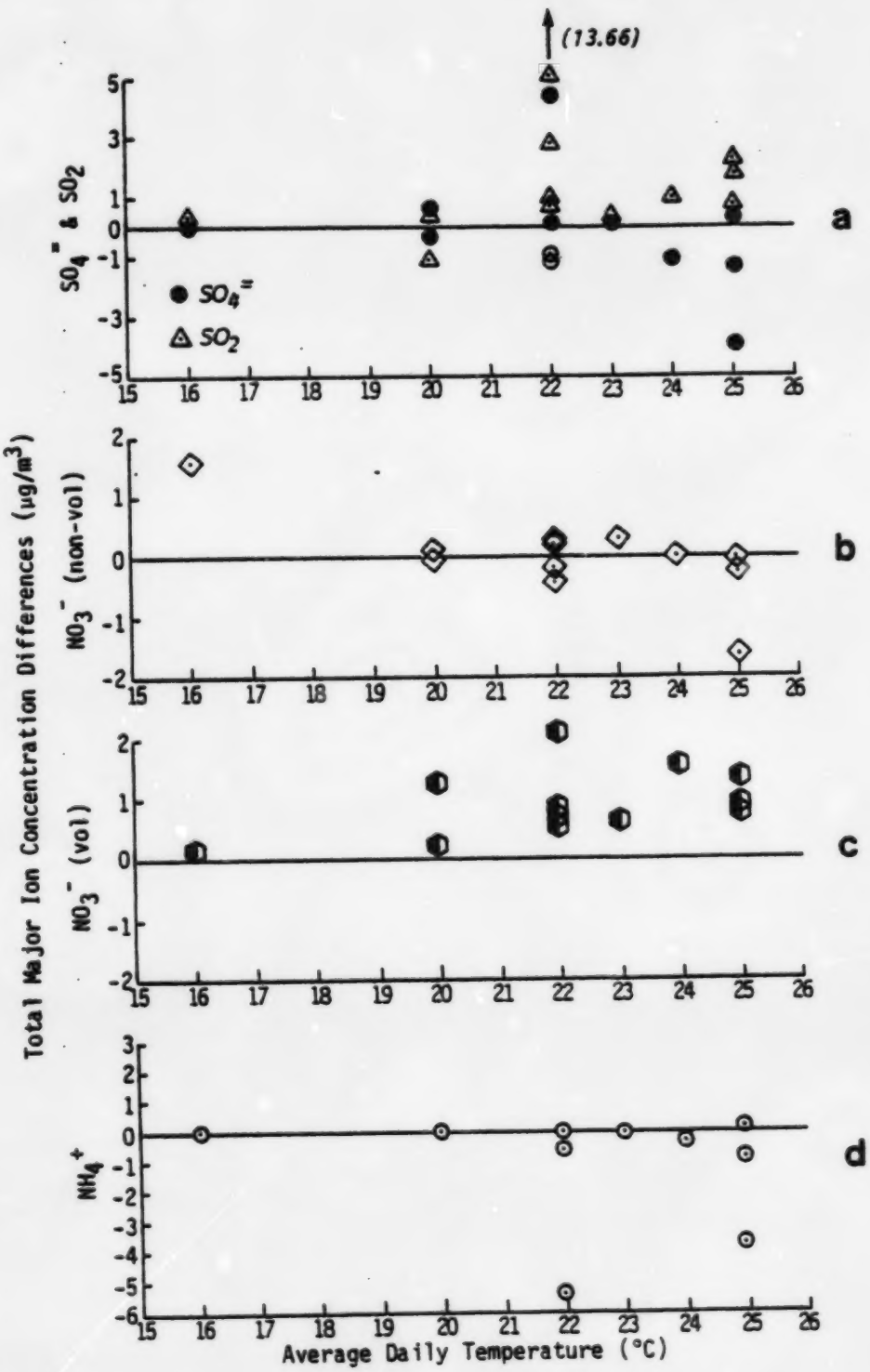

FIGURE A1

POLLUTANT CONCENTRATION DIFFERENCES (TEFLON-COATED MINUS UNCOATED DICHOTOMOUS SAMPLER) VERSUS AVERAGE DAILY TEMPERATURE (SUMMER)

164204 RD

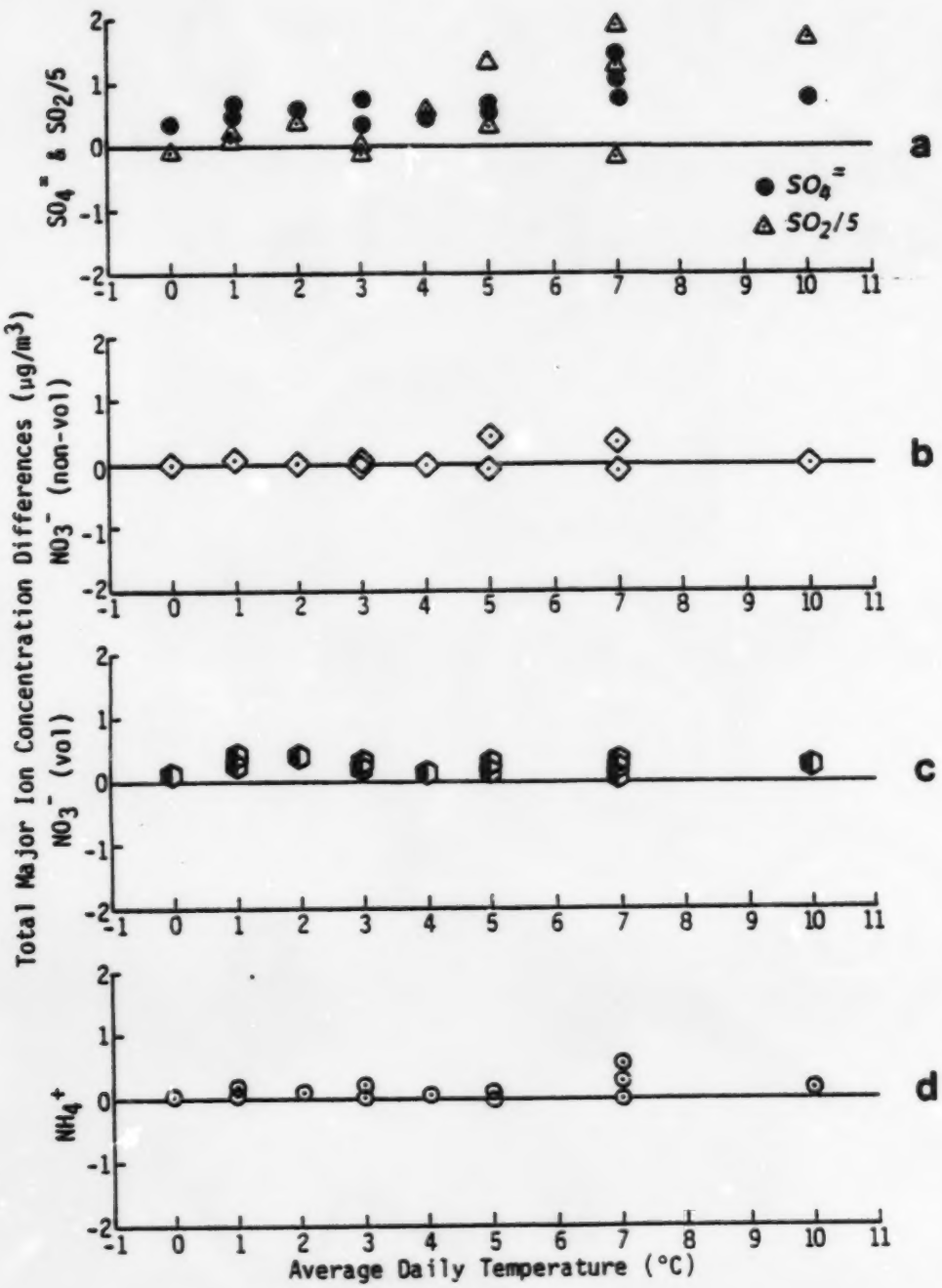

FIGURE A2

POLLUTANT CONCENTRATION DIFFERENCES
(TEFLON-COATED MINUS UNCOATED DICHOTOMOUS SAMPLER)
VERSUS AVERAGE DAILY TEMPERATURE
(WINTER)

164198 RD

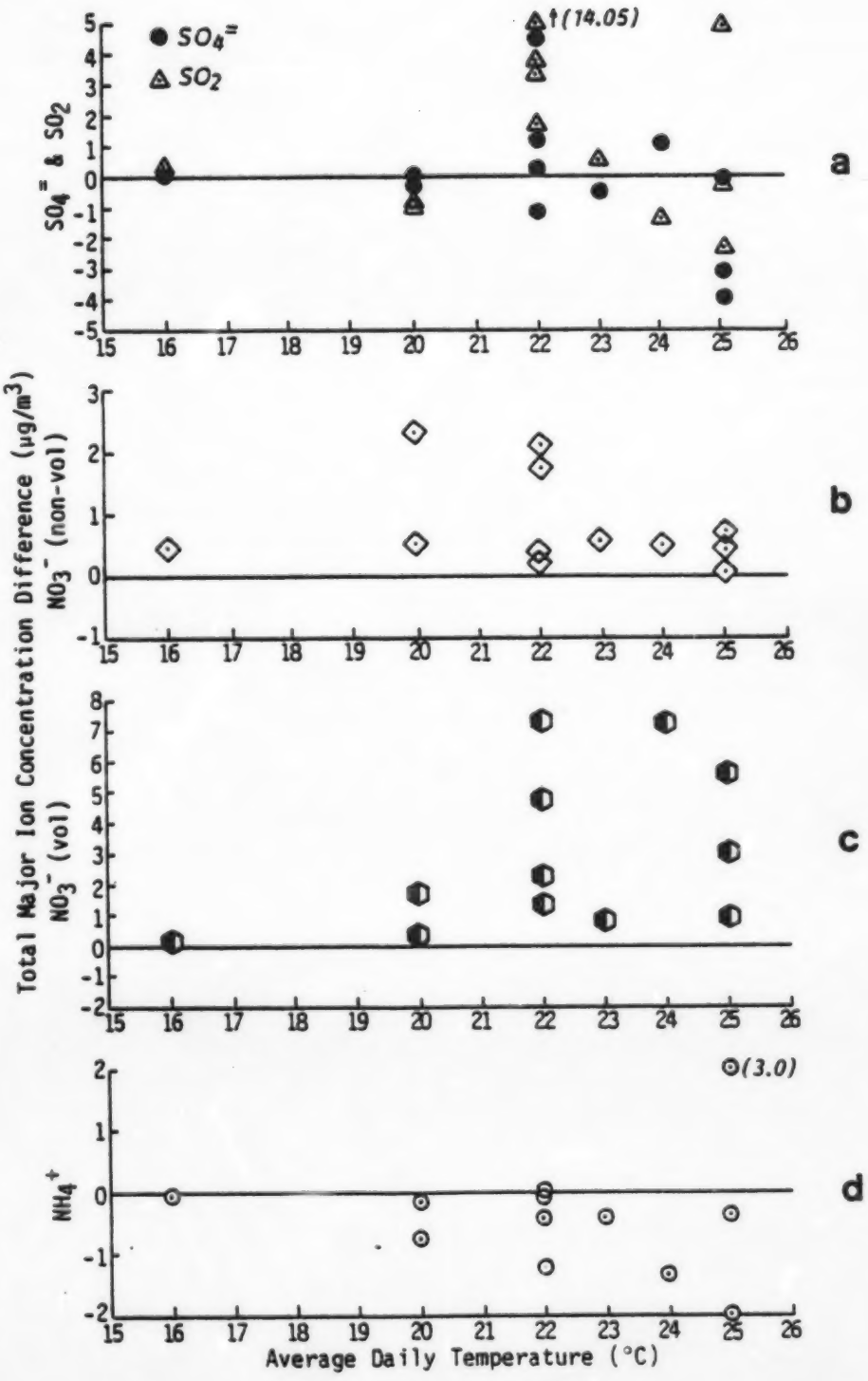

FIGURE A3

POLLUTANT CONCENTRATION DIFFERENCES (OME/AES TYPE MINUS UNCOATED DICHOTOMOUS SAMPLER) VERSUS AVERAGE DAILY TEMPERATURE (SUMMER)

164206 RD

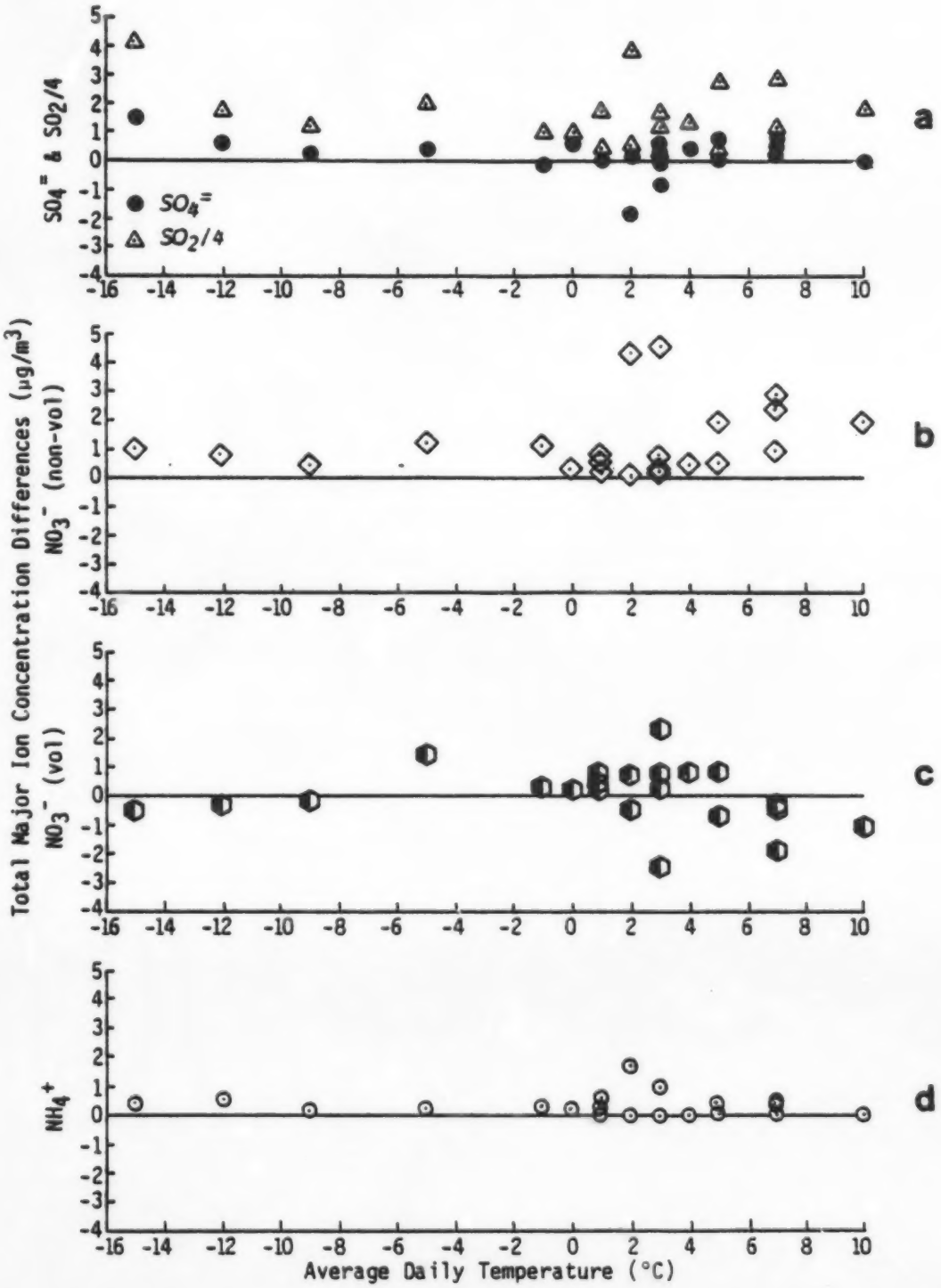

FIGURE A4

POLLUTANT CONCENTRATION
(OME/AES TYPE MINUS UNCOATED DICHOTOMOUS SAMPLER)
VERSUS AVERAGE DAILY TEMPERATURE
(WINTER)

1.64200 RD

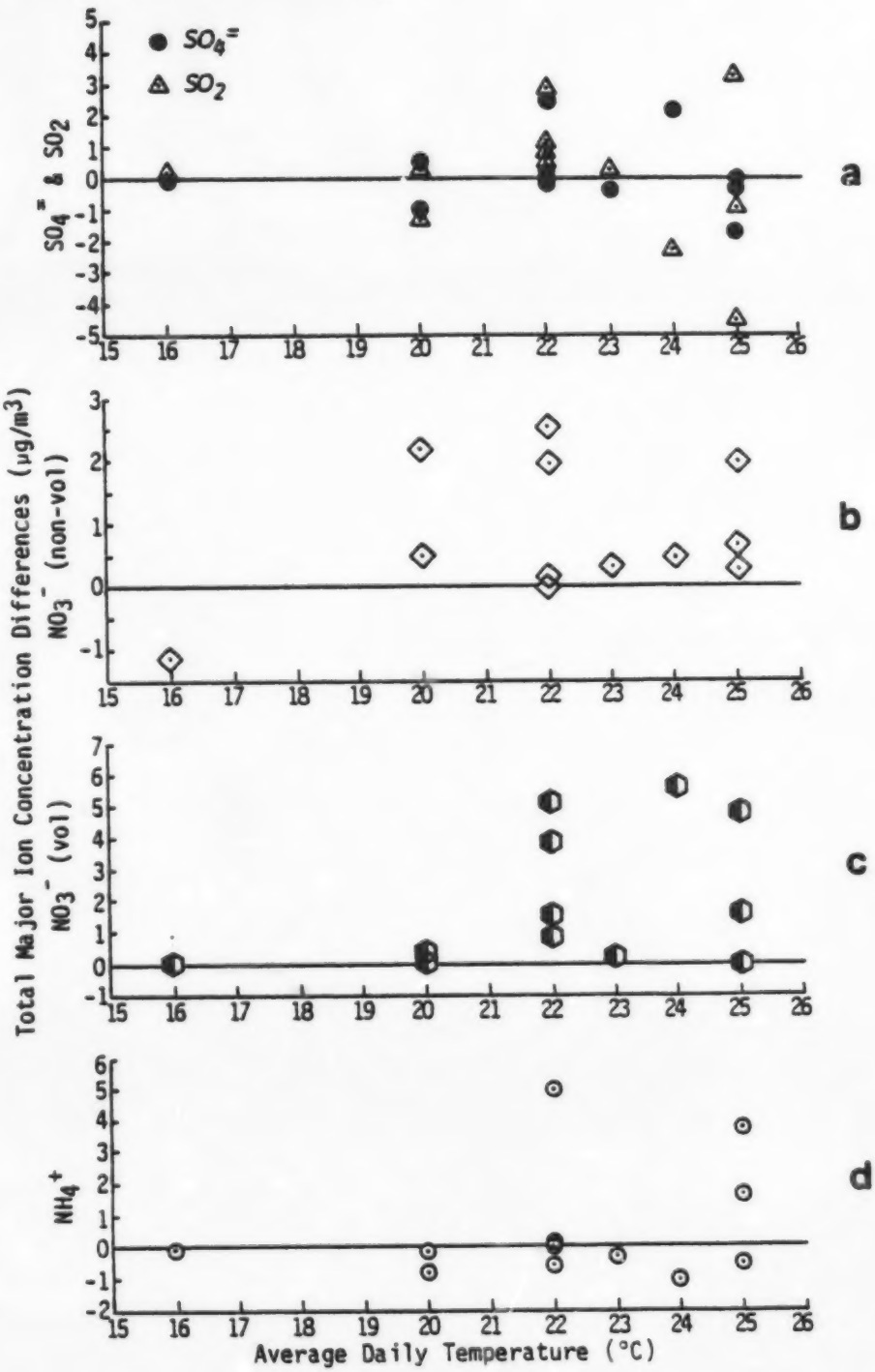

FIGURE A5

POLLUTANT CONCENTRATION DIFFERENCES (OME/AES TYPE MINUS TEFLON-COATED DICHOTOMOUS SAMPLER) VERSUS AVERAGE DAILY TEMPERATURE (SUMMER)

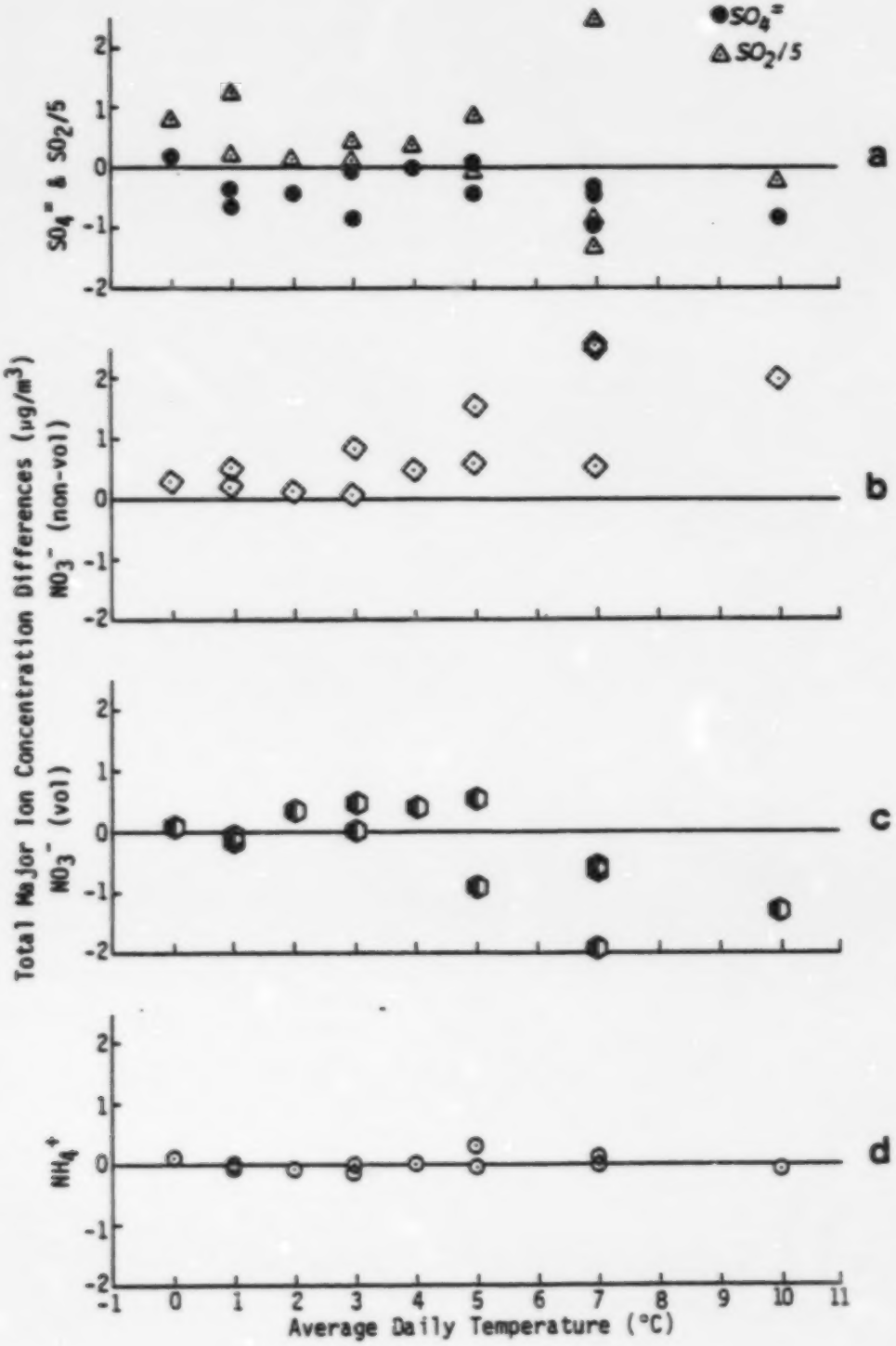

FIGURE A6

POLLUTANT CONCENTRATION DIFFERENCES
(OME/AES TYPE MINUS TEFLON-COATED DICHOTOMOUS SAMPLER)
VERSUS AVERAGE DAILY TEMPERATURE
(WINTER)

164202 RD

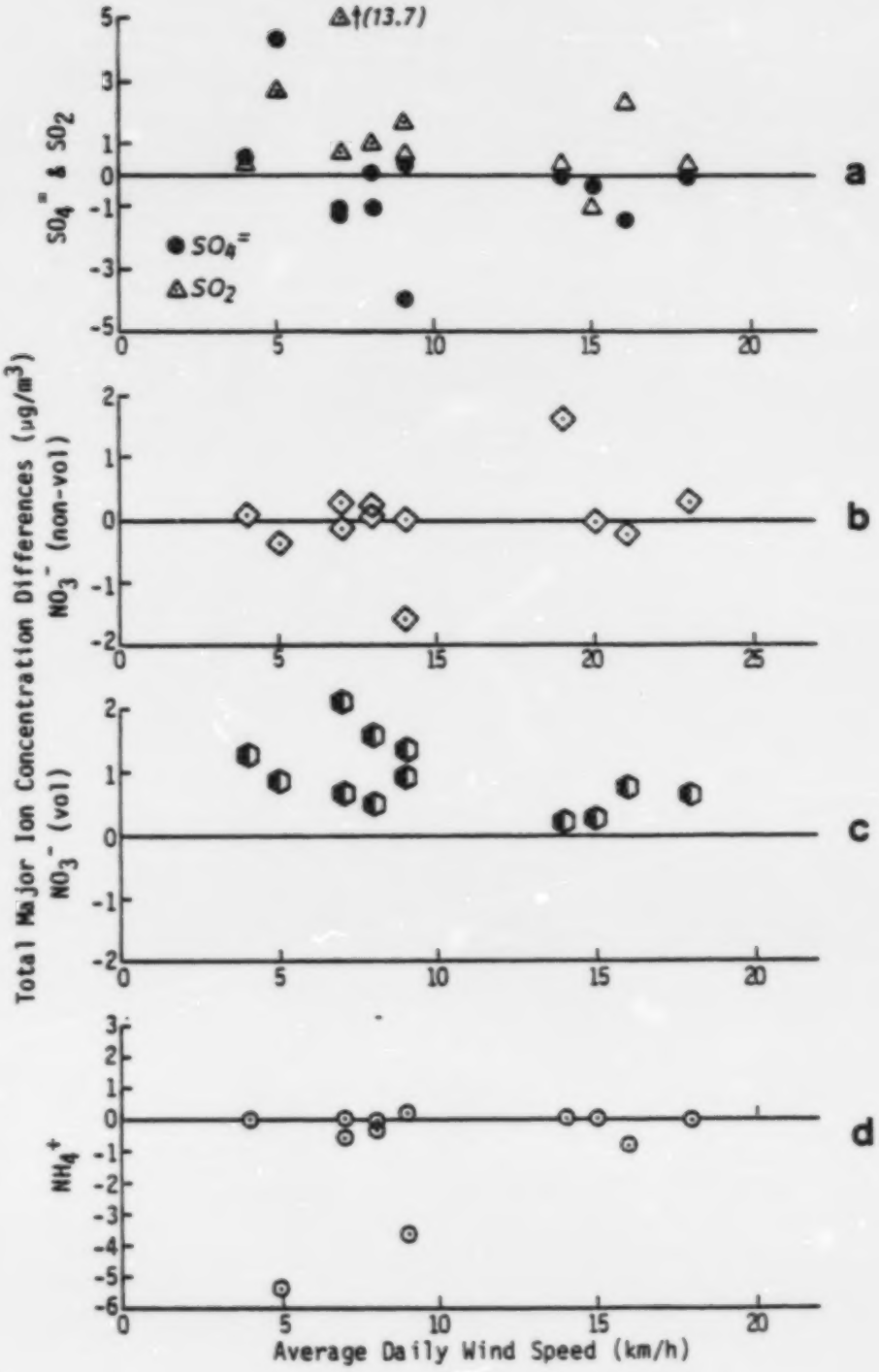

FIGURE A7

POLLUTANT CONCENTRATION DIFFERENCES (TEFLON-COATED MINUS UNCOATED DICHOTOMOUS SAMPLER) VERSUS AVERAGE DAILY WIND SPEED (SUMMER)

164205 RD

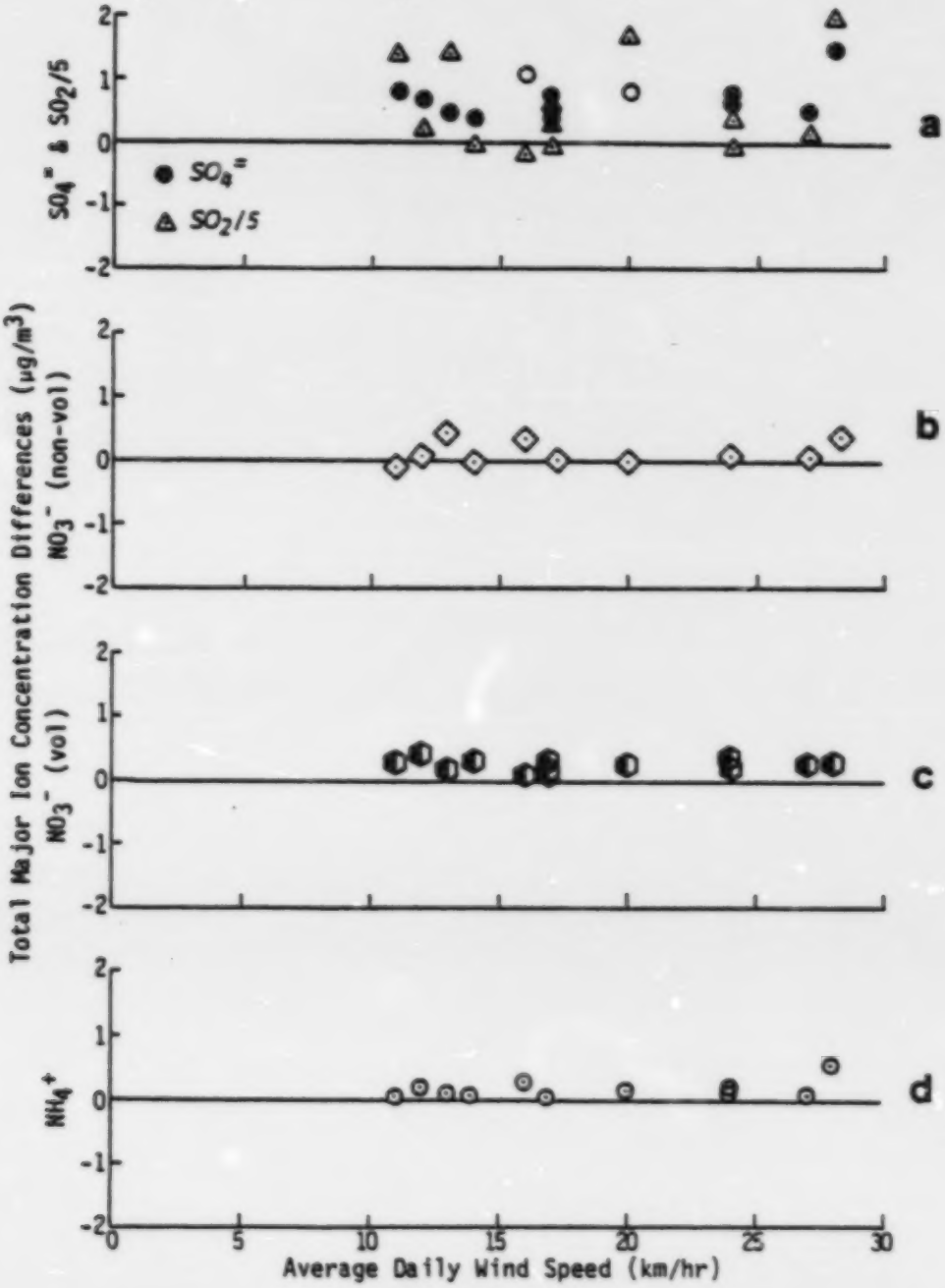

FIGURE A8

POLLUTANT CONCENTRATION DIFFERENCES
(TEFLON-COATED MINUS UNCOATED DICHOTOMOUS SAMPLER)
VERSUS AVERAGE DAILY WIND SPEED
(WINTER)

164199 RD

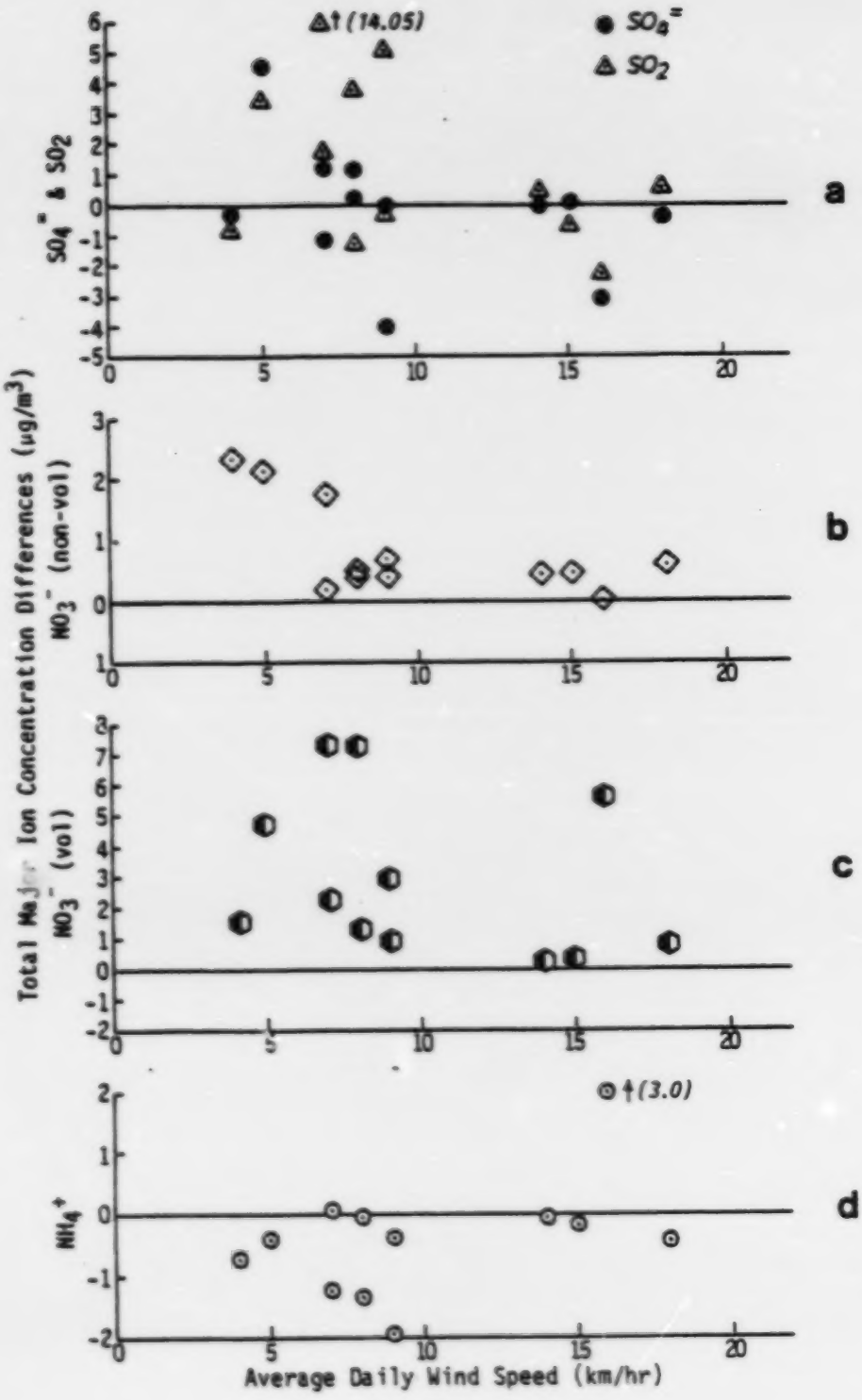

FIGURE A9

POLLUTANT CONCENTRATION DIFFERENCES
(OME/AES TYPE MINUS UNCOATED DICHOTOMOUS SAMPLER)
VERSUS AVERAGE DAILY WIND SPEED
(SUMMER)

164207 RD

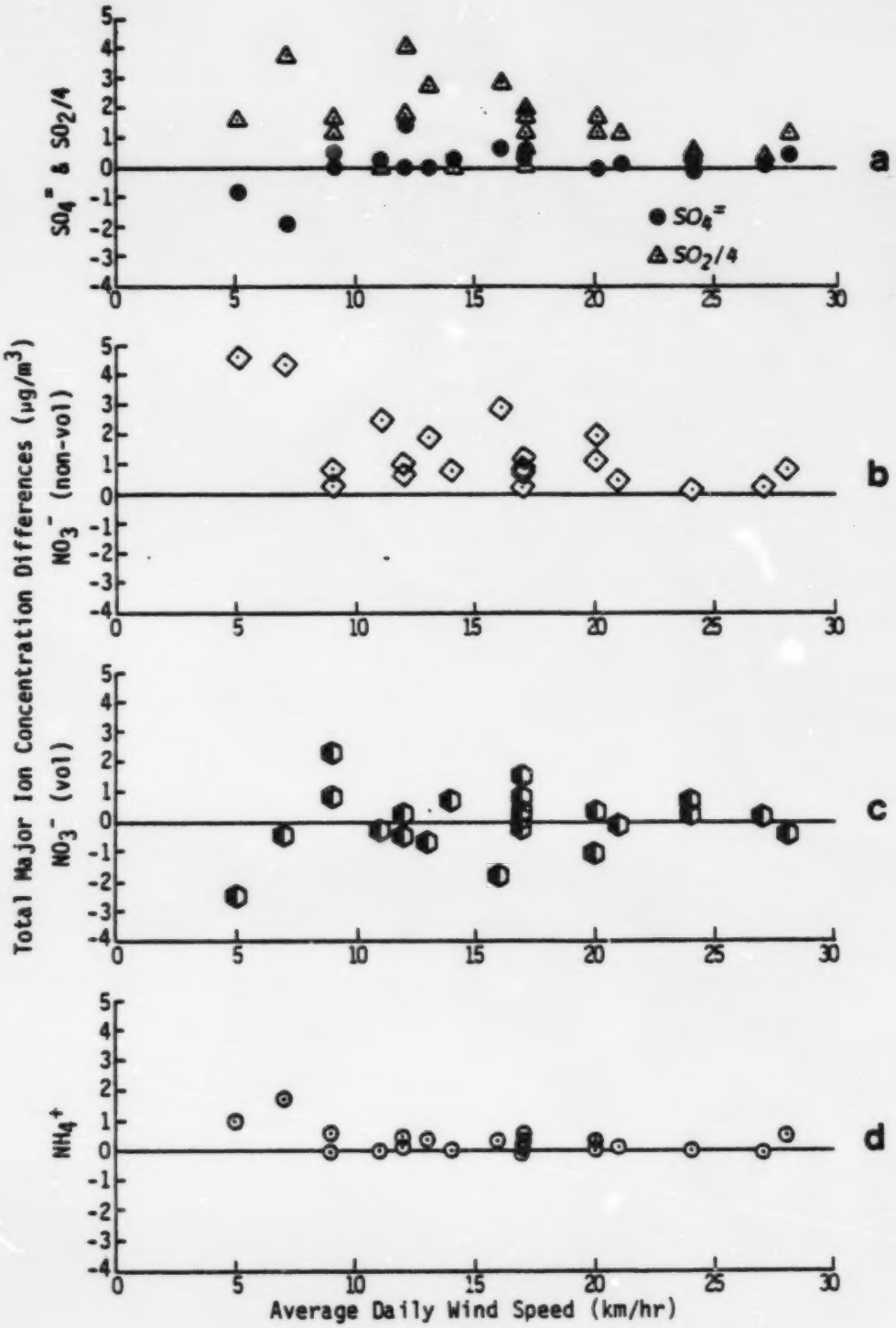

FIGURE A10

POLLUTANT CONCENTRATION DIFFERENCES
(OME/AES TYPE MINUS UNCOATED DICHOTOMOUS SAMPLER)
VERSUS AVERAGE DAILY WIND SPEED
(WINTER)

164201 RD

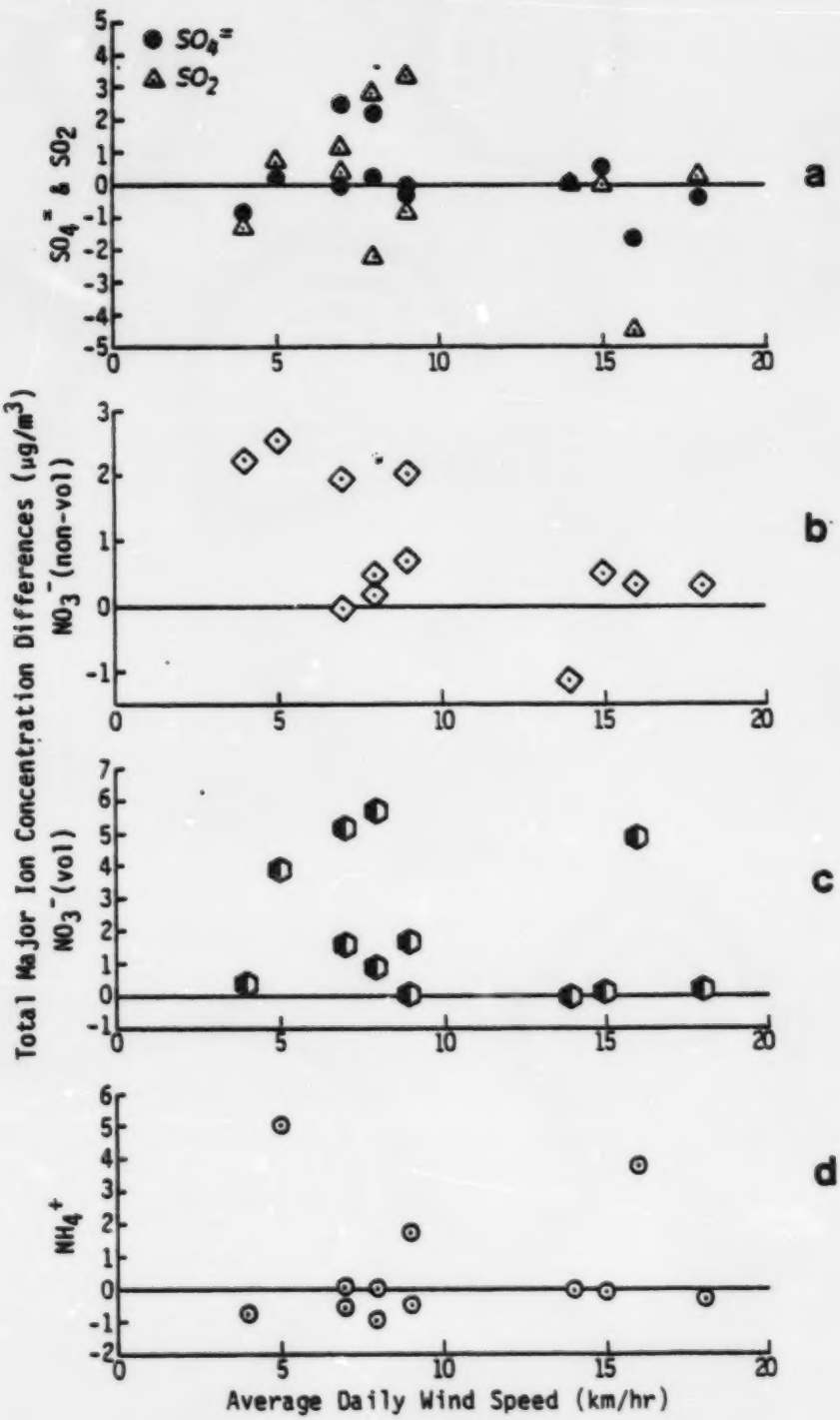

FIGURE A11

POLLUTANT CONCENTRATION DIFFERENCES
(OME/AES TYPE MINUS TEFLON-COATED
DICHOTOMOUS SAMPLER) VERSUS
AVERAGE DAILY WIND SPEED
(SUMMER)

164209 RD

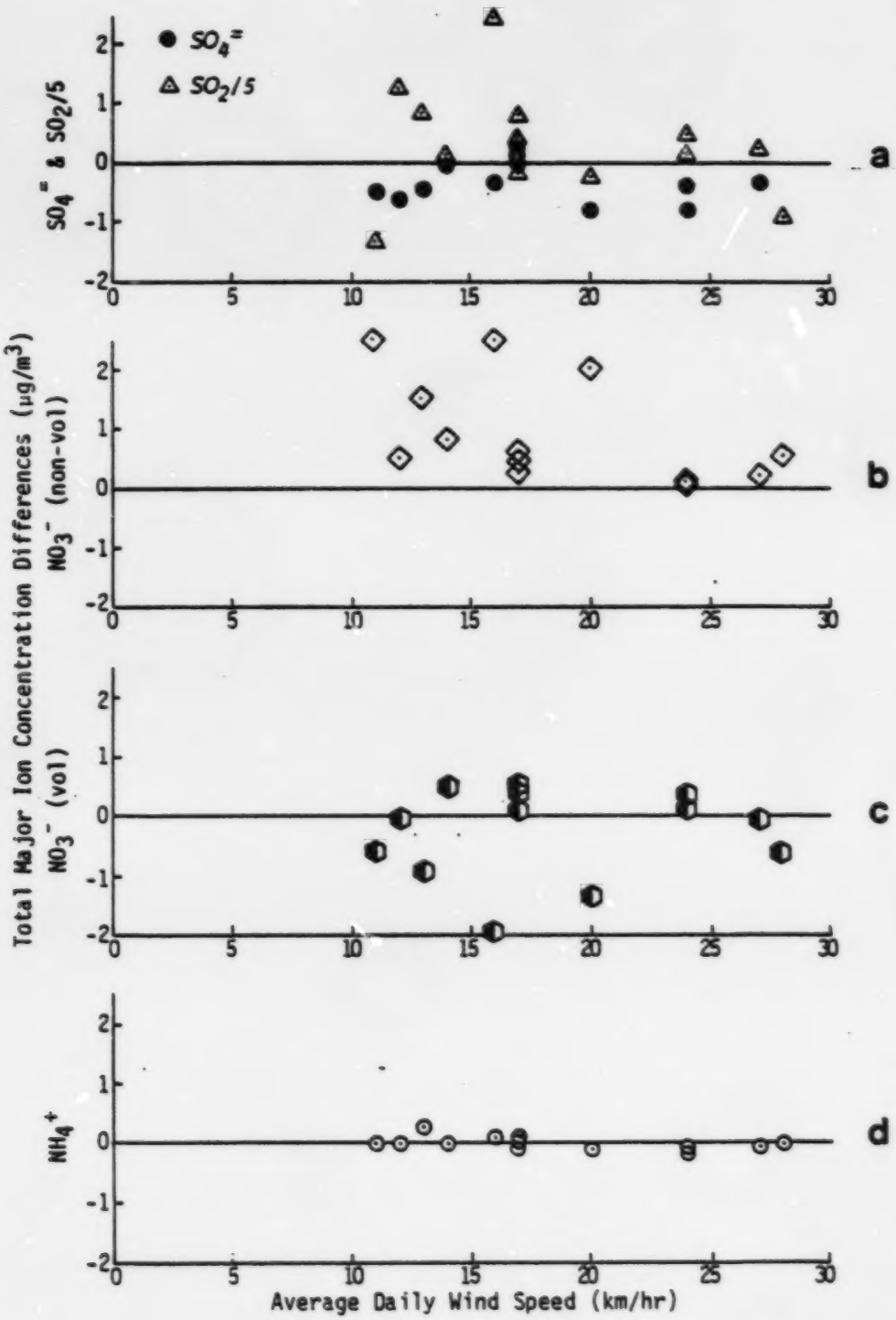

FIGURE A12

POLLUTANT CONCENTRATION DIFFERENCES (OME/AES TYPE MINUS TEFLON-COATED DICHOTOMOUS SAMPLER) VERSUS AVERAGE DAILY WIND SPEED (WINTER)

164203 RD

POOR

QUALITY

ORIGINAL